Flow Injection Atomic Absorption Spectrometry: analytical characteristics of flame AAS

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FLOW INJECTION- ATOMIC ABSORPTION SPECTROMETRY:
Analytical Characteristics of flame AAS.

by

Christina Eromowen ADEEYINWO, BSc (Hons), MSc, GRSC.

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of the University of Technology, Loughborough, UK.

November 1990

Supervisors: J. F. Tyson, BSc, DIC, PhD, CChem FRSC.
N. J. Seare, BSc, PhD, GRSC.

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In loving memory of my father,

Anthony Ebimotigha ADEEYINWO
(The Lijofi of Idepe, Okitipupa; an Ijama in Ikale.)
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ABBREVIATIONS

(I), List of abbreviations and symbols used in the text

atomic absorption
atomic absorption spectrometry
atomic emission spectrometry
atomic fluorescence spectrometry
ammonium pyrrolidinedithiocarbamate (ammonium tetramethylenedithiocarbamate)
ammonium oxalate monohydrate
centimeter
degree Celsius
dilution factor
ethylenediaminetetraacetic acid
exponential
flow injection (prefix)
flow injection analysis
gram
high performance liquid chromatography
hour
inductively coupled plasma
internal diameter
isobutyl methyl ketone
liquid chromatography
liter
micro(prefix)(10^-6)
milliliter(prefix)(10^-3)
minute
molar
nano(prefix)(10^-9)
optical emission spectrometry
polytetrafluoroethylene
relative standard deviation
second
segmented flow analysis
signal to noise ratio
ultraviolet

AA
AAS
AES
AFS
APDC
AOM
cm
°C
D.F.
EDTA
exp
Fl-
FIA
g
HPLC
h
ICP
i.d.
IBMK
LC
μ
m
min
M
n
OES
PTFE
RSD
s
SFA
SNR
UV

(II), abbreviations to Journals ................................ see Appendix (I)
ABSTRACT

Flow injection (FI) techniques for use with atomic absorption spectrometry (AAS) have attracted considerable research interest for sample introduction and calibration strategies. The interest continues in on-line preconcentration and matrix modification which are carried out by the incorporation of liquid-liquid extraction, ion-exchange, immobilised reagents, gas/vapour generation and continuous precipitation-filtration devices into suitably designed manifolds. Indirect determination of inorganic anions and organic compounds is becoming routine by FI-flame AAS. The direct analysis of solid samples, which is a shortcoming of flame AAS, was recently carried out by on-line electrolytic dissolutions. Sequential multi-element and speciation analyses have been carried out by FI-flame AAS. However, all these extensive researches still have the problem of the use of an instrument with a nebuliser system not ideal for gathering information from transient signals. Hence this research started with the characterisation of the nebuliser. The capillary tip adjustment in its barrel has a crucial point of maximum sensitivity. The absorbance for FI-flame AAS, measured as peak height, was lower than for conventional AAS with poor precision as the pumping flow rates decreased. The nebulisation efficiencies increased as the pumping flow rates decreased and were beneficial for the reduction of solute volatilisation interferences. Flow injection-flame atomic absorption spectrometry, with air compensation, offered comparable and sometimes better precision than conventional AAS. Pulse dampers were imperative for peristaltic pumps to maintain good precision at low pumping flow rates.

The depressive effects of phosphate and aluminium on the absorbance of calcium were studied. The adjustment of the instrumental parameters such as the flow rate of the fuel and burner height removed the depression due to phosphate but failed for aluminium.

On-line precipitation and filtration of basic calcium oxalate was, for the first time, effected reproducibly at room temperature and it eliminated the interference of up to 100-fold concentration excess of aluminium.

The parameters that influence on-line continuous precipitation and filtration as a method for routine analysis were studied. The use of polymer filter membranes (cheap disposable syringe filters) permitted Ca to be determined with an enrichment factor of over 800 in the range of 0 - 1 μg l⁻¹. Other analytical uses of the developed manifolds, for calibration, preconcentration and equilibrium studies, are summarised.

Key words: Atomic absorption spectrometry; flow injection; interference removal; in-line continuous precipitation and filtration; preconcentration.
PUBLICATIONS

"Flow-Injection Techniques for the Removal of Stable- compound Interferences in Flame Atomic Absorption Spectrometry of Calcium,"
Adeeyinwo, C. E., and Tyson, J. F.,

"Study of the Possible Benefits of Flow Injection Sample Introduction for Flame Atomic Absorption Spectrometry,"
Tyson, J. F., Adeeyinwo, C. E., and Bysouth, S. R.,

"Reduction of Interference Effects in Flame Atomic Absorption Spectrometry Using Flow Injection Techniques,"
Adeeyinwo, C. E., and Tyson, J. F.,

"On-line precipitation in Flow injection Atomic Absorption Spectrometry,"
Adeeyinwo, C. E., and Tyson, J. F.,

"Flow Injection Manifolds with Membrane Filters for Preconcentration and Interference Removal by Precipitation Flow Injection Flame Atomic Absorption Spectrometry,"
Debrah, E., Adeeyinwo, C. E., Bysouth, S. R., and Tyson, J. F.,
Analyst, accepted for publication.
CONFERENCE PRESENTATIONS

"A study of the interference effect of Aluminium on Calcium in flame Atomic Absorption Spectrometry,"
C. E. Adeeyinwo and J. F. Tyson;

"Interferences in flame Atomic Absorption Spectrometry,"
C. E. Adeeyinwo and J. F. Tyson;

"Reduction of Interference Effects in flame Atomic Absorption Spectrometry using Flow injection techniques,"
C. E. Adeeyinwo and J. F. Tyson;
Poster presentation, RSC meeting on Research and Development Topics in Analytical Chemistry, Plymouth Polytechnic, U. K., 18th July 1988.

"On-line Precipitation in Flow Injection Atomic Absorption spectrometry,"
C. E. Adeeyinwo and J. F. Tyson;

"On-line Preconcentration and sample clean-up using continuous precipitation and filtration in Flow Injection Atomic Absorption Spectrometry,"
Adeeyinwo, C. E., Debrah, E., and Tyson, J. F.;
CHAPTER ONE

FLOW INJECTION - ATOMIC ABSORPTION SPECTROMETRY

1.1. INTRODUCTION

The present day automation of an atomic absorption spectrometer involves the use of microcomputers/microprocessors to control the instrument, collate and analyse data and possibly generate reports. A typical instrument for laboratory processes would have the operating parameters such as slit width, wavelength, lamp current, burner height and flow rates of fuel and oxidant fed into it, at the touch of a button.\\textsuperscript{1,2} The optimised parameters as well as the details of the analytical method can be stored. The results of the analysis, in concentration units, can be calculated by the computer. When dealing with a few samples, the introduction of the samples to the spectrometer may be manual. However the introduction of a large number of samples as needed in clinical, agricultural laboratories and in process monitoring, requires automation of the sample introduction to quicken the analysis and, at the same time, eliminate human error. Thus a modern flame atomic absorption spectrometer, designed as an automated system, can determine six elements in 50 samples in less than 35 minutes, a throughput of about 500 per hour.\\textsuperscript{3} Such an instrument has an automated sample introduction capability.\\textsuperscript{4-7} Some instruments, especially in process monitoring, are computer intelligent, that is, they flag faults and rectify them accordingly.\\textsuperscript{8,9} Although the system described in reference 8 used ICP-OES detection, it should be feasible to be operated with an atomic absorption detection.

Analytical automation dates back to the 1950's and 1960's when a variety of continuous analysers using detections such as refractometry, gas chromatography, potentiometry and infrared spectrometry were developed for process streams. Instruments such as auto-titrators, elemental analysers and continuous flow analysers featured in the laboratory. The classification of automated analysers is yet to be standardised;\\textsuperscript{10} so in this report, automated analysers are classified, based on their design and method of operation, into batch (discrete) and continuous flow analysers.

In the discrete analyser, the samples are put into series of containers (test tubes or
mini-beakers) on a conveyor belt where the normal stages of conducting a manual analytical testing such as reagent addition, stirring and analyte measurement are performed on each sample as it moves past the dedicated robot arms along the belt. Thus each sample is handled as a separate entity and a specific test is carried out at any time. This makes the analyser very selective. However the instrumentation has many mechanical moving parts and as a result, the installation and maintenance costs are quite considerable. The variants of discrete analyser which use pre-packed reagents in plastic bags (marketed by DuPont) or thin films of reagents on slides (produced by Kodak) give more flexibility in that they allow multiple tests on a sample. The rapid rotation of samples past detectors, as performed in centrifugal analysers, offers a means of running the same tests on many different samples. Different assays can be carried out rapidly on the same sample as the mixing is done by the centrifugal force generated in the system. All these variants add complexity to the instrument such that the cost of a discrete analyser may range from 35,000 to over 200,000 US dollars. The sample throughput is low compared with continuous flow analysers as it is often less than 12 samples per hour.\textsuperscript{11}

In continuous flow analysis, the samples are analysed as flowing streams of fluid so that the analyser always has a pumping system. The procedural operations of chemical testing such as filtration, dilution, reagent addition and mixing can be performed in the flowing streams prior to the measurement of the analyte by a flow through detector. The first commercial continuous flow analyser is based on the invention of Skeggs.\textsuperscript{12,13} The analyser operates with air segmentation in all its flow streams and the methodology is appropriately termed segmented flow analysis (SFA). In this analyser, the capillary tube through which the solution (standard, reagent or wash) is aspirated for the flow stream, lifts periodically from the solution to aspirate air. Solution containers are arranged in order in a tray and the aspiration time is controlled. Segmented flow analysis reduces reagent consumption, improves sample throughput and allows different serial assays be performed, for the pump head can be made to accommodate many flow streams. The addition of air is used: (a), to limit sample dispersion; (b), to minimise carry-over and cross contamination between samples; and (c), to aid mixing so that reactions can attain steady states. The sandwiched air pockets, however, cause increased pulsations in the flow streams as well as disturbing analyte measurement.\textsuperscript{14} Hence streams have to be de-bubbled prior to the flow cell. De-bubbling is also necessary whenever there is a re-pumping in order to maintain bubble size control in the system. The advantages of SFA are well demonstrated in the varied models of auto-analysers marketed by Technicon Instrument Corporation of USA (1957 - 1981 models).\textsuperscript{10} The electronic
gating of the detector (bubble gating in the flow cell) was incorporated into the design of the segmented flow analyser to overcome the drawbacks.\textsuperscript{15,16} The outcome is a system with increased complex instrumentation and costs. The more recent development in the methodology of continuous flow analysers is flow injection analysis (FIA).\textsuperscript{11} Flow injection analysis as an alternative to SFA, operates without air segmentation in the flow streams and so sidesteps the problems of air bubbles. The operation of the different analysers is shown in Fig. 1.1.

Fig. 1.1. Basic operation of the different types of automated analysers: (I), discrete, belt-type; (II), continuous flow, air-segmented; and (III), continuous flow, flow injection. P, pump; C, carrier stream; R, reagent; S, sample port; V, valve; M, mixing stage; D, detector; and W, waste.
Flow injection analysis features the injection of micro volumes of sample solutions into a carrier flow stream which offers increased sample throughput over SFA. The additional merits are: (a), the controlled and reproducible timing of reactions does not have to attain steady state for a valid measurement to be made; (b), relatively easier startup and shutdown procedures of the analyser system than SFA; and (c), the instrumentation, whether at installation or during maintenance, is of lower costs.

The theory and practice of FIA has shown that FIA caters for virtually all forms of chemistries and sample throughput. However, most FIA apparatus is still largely of the "do-it-yourself" variety in the teaching or research laboratory. The manufacturers of FIA analysers, at present nine in number, produce flow injection analysers suitable more for teaching and research than for process streams; a flow injection analyser for real time monitoring is yet to appear on the market.18-20

The reported successes of FIA for general analytical purposes, is demonstrated by the publication of books, reviews and scholastic articles which approached two thousand in number in twelve years (1975 - 1987).21 At present, the number of books/monographs dedicated to the practice of FIA is ten as well as a journal in Japanese. The relevant books that use English as the literary language are shown in Appendix II. This outweighs the number of publications reported for other variants of continuous flow analysis such as 'controlled dispersion'22 and 'air carrier'23,24 continuous flow analysis. The historical emergence of FIA, began in 1975 when Ruzicka and Hansen (working in Denmark) coined the term Flow Injection Analysis (FIA).25 It was originally intended for serial assays so they described it as a new concept in fast continuous flow analysis. The principles and theory of FIA evolved through the various collaborative studies amongst the early workers such as Stewart, J. W. B. (USA), Bergamin and Zagatto (Brazil), and Betteridge (England).26-31 As of 1985, the practice of FIA was fully developed in countries such as China, Japan, and Spain, as shown by articles in the special issue of "Analytica Chimica Acta."32 The publication expressed the views of thirty six authors (from ten countries) on the merits of FIA. At present, the definition of FIA is generalised to encompass all detection systems as:

"Information - gathering from a concentration gradient formed from an injected, well defined zone of a fluid, dispersed into a continuous unsegmented stream of a carrier."11

In 1979, Zagatto et al.33 (Brazil) and Wolf and Stewart34 (USA), used FIA as a means of fast sample introduction for atomic absorption spectrometry. The resulting
coupling was termed, by the first group, flow injection atomic absorption spectrometry (FI-AAS). Since then, FIA has increasingly become a method of sample introduction for atomic spectrometers. This is due to the high precision, high sampling rate, variable scaling of flow injection apparatus and most of all, on-line sample treatment schemes which enhance the sensitivity and at times, improve the detection limit of these instruments. This is specially so for flame AAS. The number of FI-AAS publications was about 160 at the end of 1986 and this amounted to roughly 12 percent of the total papers on FIA as shown in Fig. 1.2.

![Diagram of FIA publications at the end of 1986](image)

**Fig. 1.2.** FIA publications at the end of 1986.

The number of reviews on FI-AAS which were then fifteen, has now increased to twenty and there is a book, included in Appendix II, solely devoted to flow injection atomic spectrometry (FI-AS). The realisation that FI-AAS requires a specially designed nebuliser interface to gain the full potential of the coupling should continue to generate interest in the field. There is some controversy concerning the best mode for operating the FI-AAS system. So far, Tyson and his research group have studied several applications and the theory of FI-AAS that they have successfully developed the techniques for instrument calibration in flame
AAS.545-53 Other works such as on-line extraction, precipitation and ion-exchange in which a low flow rate is accommodated by the atomic absorption spectrometer, have allowed preconcentration, matrix modifications, and anion analysis.454-69 On-line vapour generations,70-73 as well as serial coupling of UV-visible spectrophotometry74,75 and voltammetry76,77 with flame AAS have been made possible through FIA. In the same vein, attempts are being made to couple both liquid chromatography (LC) and high performance liquid chromatography (HPLC) to flame AAS.78-80 All these couplings aim at conducting speciation studies using atomic absorption spectrometer as the element specific detector.

1.2. FI-AAS PRINCIPLES AND INSTRUMENTATION

The apparatus for FI-AAS consists of plastic tubings (internal diameter 0.4 mm to 1.0 mm) to contain the streams, pumps to propel the fluids and injection ports where precise volumes of samples are metered and intercalated into the carrier stream. Additional components such as end-fittings and coupling connectors, are necessary to make leak-proof connections. The resulting connections, when linked to the atomic absorption spectrometer, constitute the manifold.

Fig. 1.3 shows some of the manifolds used in FI-AAS.37,40 They range from the single line type for presenting samples to the spectrometer, to the more complicated designs for merging zones, zone sampling and countercurrent flows that are used for sample treatments prior to nebulisation. For the rational design of manifolds, the controlled and precise dispersion characteristic of FIA is quantified in terms of dispersion coefficient (D). This quantity is theoretically derived from the concentration-time profile of a sample plug which undergoes only physical processes of zone dispersion in a single line manifold as shown in Fig. 1.4.

Thus,

\[ D = \frac{C_0}{C_m} \] .......................................................... 1.1

where \( C_0 \) is the original analyte concentration and \( C_m \) is the analyte concentration at peak maximum.

If the instrument response is directly proportional to the analyte concentration (which is usually assumed) then,

\[ D = \frac{A_0}{A_m} = \frac{H_0}{H_m} \] .......................................................... 1.2

where \( A_0 \), \( A_m \), \( H_0 \) and \( H_m \) are steady state absorbance, peak absorbance, steady state recorder height and recorder peak height respectively.
Fig. 1.3. Manifolds used in FI-AAS.  
(i), single line manifold; (ii) to (ix), complex manifolds of which (iii) is a typical merging zone; (vii) is a typical pulsed elution; (viii) is a typical zone sampling; and (ix) is a counter current mode of elution. 
C, carrier stream; I, injection point; O, organic phase; P, pump; PBR, packed bed reactor; PS, phase separator; R, reagent stream; S, sample solution; and W, waste.
Fig. 1.4. (i), Schematic diagram of single line manifold; (ii), concentration - time profile in a carrier tube; (iii), instrument response.

$C_0$, original analyte concentration; $C_m$, concentration at peak maximum; $S$, sample injection; $T$, residence time; $H_m$, FIA peak height; $H_0$, height corresponding to steady state; $W$, peak width at a selected level; $A$, peak area; and $t_b$, peak width at the base line.

Peak area and peak width have also been used to quantify the instrument response.

The dispersion of the sample zone changes as the carrier dimension (tube length and inner diameter) or flow rate or volume of the sample zone change. The exact quantification of these variations has been propounded using the theory of flows in tubular conduits. This invariably employs a mathematical treatment and the use of models such as the single mixing tank or tanks in series. The results are mathematical expressions which may be complex; and where simple, the equations do not represent the entire observed behaviour of the manifold especially if the
manifold contains packed columns, tightly coiled tubes or gradient tanks. This limitation can be due to one or more of these factors:

(i), whenever a reaction occurs in the manifold (which is often the case), the formation of the product to be measured may be limited by kinetic factors or the product may decompose;

(ii), the relationship between concentration and instrument response may not be linear, as a result the ratio $C_0 : C_m$ would not be equal to $H_0 : H_m$; and

(iii), the response time of the measuring and recording circuitry may distort the peak shape. This distortion worsens as "damping" is increased especially at high flow rates and at high concentration of the analyte.

Whilst factors (ii) and (iii) can be ignored for other FIA detectors, they are important for flame AAS because there are many processes involved when the nebuliser-burner system converts liquid into gaseous atoms. Also, the nebuliser-spray chamber-burner system possesses considerable dead volume which compounds the dispersion of the sample zone and this effect varies from one nebuliser design to another. The performance of nebuliser systems has been critically studied by several workers such as Browner, Cresser, Gustavsson, and Sturman with the aim of achieving optimum design for nebulisers. Gustavsson described a nebuliser interface that improved nebulisation efficiency to 100% at a low flow rate of 2 ml min⁻¹ (normal nebulisation efficiencies for ICP-AES is about 1% and flame AAS is about 10%). The interface has been successfully adapted for FI-AAS with the advantage of a twelve fold improvement in detection limit. However, a computer-based smoothing of the signal was needed to bring the precision close to that of the normal nebuliser at 5%.92

At present, the standard approach to designing an FI-AAS manifold starts with a carefully optimised AAS instrument. Further optimisation of the manifold with respect to pumping rate, sample volume and tube size then depends on the dispersion necessary to attain the best result for a given procedure. Hence the dispersion of the manifold is classified into reduced (D <1), limited (D = 1 to 3), medium (D = 3 to 10) and large (D >10). Table 1.1 shows the basic design features that could lead to the different dispersions. The single bead string reactor of Reijn et al.,93 the three dimensional knitted reactor of Engelhardt and Klinkner94 and other similar variants, would be classified as medium dispersion designs. However, there are yet no reports of their application in FI-AAS. These reactors are claimed to provide decreased peak tailing and short residence times hence increased sample throughput compared with the same length of straight or loosely coiled open tubular reactor.
Table 1.1. Classification of FIA manifolds

<table>
<thead>
<tr>
<th>FIA system</th>
<th>Degree of dispersion</th>
<th>Basic design feature</th>
<th>Application</th>
<th>Response profile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced dispersion</td>
<td>&lt;1</td>
<td>microcolumn</td>
<td>preconcentration to enhance sensitivity</td>
<td></td>
</tr>
<tr>
<td>Limited dispersion</td>
<td>1 to 3</td>
<td>straight tube of short length.</td>
<td>automated direct sample introduction</td>
<td></td>
</tr>
<tr>
<td>Medium dispersion</td>
<td>3 to 10</td>
<td>long tube or packed bed</td>
<td>standard additions and reaction purposes</td>
<td></td>
</tr>
<tr>
<td>Large dispersion</td>
<td>&gt;10</td>
<td>mixing chamber</td>
<td>sample dilution especially electronic dilution</td>
<td></td>
</tr>
</tbody>
</table>

Nebuliser suction in flame AAS has been used to propel the carrier stream in FI-AAS. The performance is not as precise as the use of an external pump because nebuliser suction is sensitive to viscosity changes that may occur in the different samples; or to any flow obstruction, however minute. The ingress of air that may occur at the connectors and the possible degassing in the liquid streams also give erratic signals. The peristaltic pump, with incorporation of pulse dampers has been of wide use in FI-AAS. The aforementioned problems are alleviated when these pumps are used. In addition, the pump head (changeable in some designs such as that of the Gilson Minipuls) can accommodate two or more flow streams hence, many different sample pretreatments can be performed prior to nebulisation. The use of pump tubes of different internal diameters (i.d.s) affords a
wide range of flow rates. The problem of roller pulsation is overcome with the use of dampers and manifold operation with flow rates below the normal aspiration rates of the nebuliser is often carried out with a flow compensation close to the nebuliser inlet. This procedure improves precision.\textsuperscript{100,101} Different brands of peristaltic pumps such as the Gilson Minipuls, Ismatec mini-pump, Alitea and Watson-Marlow pumps have been of use in FI-AAS.\textsuperscript{48,77,102} Other flow propelling systems such as syringe pumps,\textsuperscript{52} gas-pressurised reservoirs,\textsuperscript{97,103} and HPLC low pressure reciprocation pumps\textsuperscript{4,96,101,104} have also been of application though to a small extent.\textsuperscript{40}

Sample injection into the FI- flow stream is such that precise volumes are metered and intercalated into the carrier stream. The commonest device used for this purpose is the rotary valve, similar to those originally designed for use in liquid chromatography (LC). The operation of the valve is shown in Fig. 1.5 and it can be performed with a precision of less than 2\% RSD.\textsuperscript{105}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.5.png}
\caption{FIA sample injection: operation of a six-port rotary valve to inject a sample plug into a flowing stream of carrier.}
\end{figure}

Other injection devices are slider (or commutator) valves and the use of a pump to aspirate a sample for timed periods in a "controlled dispersion" mode. The latter options of injection are particularly amenable to computer control. In addition, a fixed volume of sample solution can be metered into a conduit to be propelled by the carrier stream using the alternated pumping of two pumps. The pumps operate at "stop" and "go" sequence. The entire operation is called hydrodynamic injection\textsuperscript{106} and it has been applied in FI-AAS by Zagatto et al.\textsuperscript{107} The workers isolated the sampling stage from the influence of the nebuliser suction with the use of either a commutator or two Y- connectors to sandwich the sample conduit. They reported the precision of this mode of injection as comparable to that of rotary valves only at pumping flow rates that are greater than the nebuliser liquid suction. Otherwise, the
Metered sample volumes are prone to diffusion error. This observation is supported by Harrow and Janata\textsuperscript{108} who carried out a comparative study of hydrodynamic and valve injections. They reported hydrodynamic injection to be less precise than manual rotary valve. In addition, they found slider valves to have maintenance problems and to be expensive whereas solenoid valves were reliable and relatively cheap.

The different pumping devices, injection techniques and tubing materials for FI-AAS have been covered in a review by Tyson.\textsuperscript{40} Developments in the construction and ingenious application of valve systems are such that Jorgensen et al.\textsuperscript{109} recently devised a rapid switching multifunctional valve actuated by means of compressed air from a laboratory line. The valve could also carry out double loop sampling and ion-exchange preconcentration in one or two columns. Electronically operated devices used for loop-based, time-based hydrodynamic, sequential and nested injections have been described by Krug et al.\textsuperscript{110} A manually operated six-port rotary valve for performing all the aforementioned operations and more, has been reported by Erickson et al.\textsuperscript{111} Further arrangements of two or more valves have also been applied in speciation\textsuperscript{112} and kinetic studies.\textsuperscript{113} A recent report by Lazaro et al.\textsuperscript{114} gives information on the advances in the pumping and sampling devices in FIA which are also of interest in FI-AAS.

1.3. FI-AAS APPLICATIONS

Flow injection atomic absorption spectrometry has expanded its scope from just a precise means of introducing and diluting the samples that are difficult to nebulise conventionally to a means of performing rigorous solution chemistry prior to nebulisation. This scope has recently extended to trace and ultratrace analysis because FIA provides a closed system that avoids sample contaminations. Also the carrier stream allows bracketing-blank measurements that would give accurate determinations. In short, FIA offer the potentials for improvements in virtually all stages of the analytical method in both AAS and ICP-AES.\textsuperscript{35,115,116} The notable reported applications so far are in the following areas.

1.3.1. Sample Introduction

Olsen et al.\textsuperscript{103} used the commercial flow injection analyser, FIAstar,\textsuperscript{117} to analyse samples of seawater of 3.3 percent salinity. Sample volumes of 150 µl were
injected into a distilled water carrier stream to a flame atomic spectrometer. A single line manifold was used and this allowed Cd, Pb, Cu and Zn to be determined in the concentration range, 0.1 - 10 mg l\(^{-1}\), with a throughput of 180 - 250 h\(^{-1}\). No burner blockage was observed.

Using a single line manifold, Attiyat and Christian\(^{118}\) safely fed organic solvents into the flame AAS. The authors used methanol, ethanol, acetone and isobutyl methyl ketone (IBMK), in turn, as a carrier stream and as the sample solvent for the determination of Cu. At a pumping rate of 8 - 9 ml min\(^{-1}\), they showed that acetone is the best sample solvent whilst IBMK is the best carrier stream. This solvent combination afforded a sharper peak than water with an attending eight-fold enhancement and a precision of 2.3 percent. Attiyat, in a later work,\(^{119}\) showed that flow rate optimisation is necessary to attain an enhancement in the determination of Cu. In this report, pentanone was the sample solvent and methanol was the carrier stream. The combination afforded a ten-fold enhancement over water. Also, Taylor and Trevaskis\(^{120}\) determined Pb in gasoline with a precision of 1 percent. Acetone was used as a carrier stream and IBMK as the sample solvent. Indeed, Brown and Ruzicka\(^{97}\) and Garcia et al.\(^{100}\) showed that sample introduction by FIA offers better precision than conventional aspiration and when the pumping rates are a bit higher than the normal nebulisation suction rate, one may obtain a higher sensitivity depending on the type of nebuliser. Better precision may also be obtained at low pumping rates if these rates are augmented with air prior to the nebuliser.\(^{96}\) However, these improvements not only depend on the type of nebuliser but also on the adequate minimisation of carrier stream noise of which a major contribution stems from the pumping system.\(^{43}\)

### 1.3.2. Calibrations/dilutions

The calibration and dilution methodologies used in FI-AAS depend on the nature of sample (neat or requiring treatment) as well as the estimated concentration of the analyte, and the result is the design of various manifolds.\(^{121}\) Thus, the manifold designs for normal calibration purposes range from merging zones,\(^{53}\) variable tube dispersions\(^{52}\) and networks\(^{53}\) to time based injections. The time based injections may be used to effect zone sampling\(^{122}\) or to aspirate very small volumes, typically 1-5 \(\mu l\),\(^{56}\) into a carrier stream. All these modes offer discrete dilutions of samples. The incorporation of a mixing chamber into the manifold offer both discrete\(^{102,123}\) and continuous\(^{124}\) dilutions of samples which are applied for normal calibration
purposes. Also, manifold designs for reversed-FIA\textsuperscript{45} and zone penetration\textsuperscript{125} have been used to effect calibrations by the standard additions method. A brief description, with comments, of these methods are presented as follows:

Tyson and Appleton\textsuperscript{50,124} injected a standard solution into a water carrier stream having a well-stirred, mixing chamber close to the nebuliser of a flame atomic spectrometer. This generated an exponential concentration-time profile which was fitted with Equation 1.3

$$C_t = C_m [1 - \exp(-u/t/V)]$$ \hspace{1cm} 1.3

where $C_t$ is the concentration at any time, $t$; $C_m$ is the concentration of the standard solution; $u$ is the pumping rate and $V$ is the volume of the mixing chamber.

The absorbance-time response of the spectrometer to the continuously varying concentrations, was recorded (on chart or by computer). Sample solutions were then pumped at the same flow rate but bypassing the chamber to give steady state absorbance. The corresponding times for the steady absorbance were read off the absorbance-time profile and substituted into Equation 1.3 to obtain the concentrations of the sample solutions, $C_s$ ($= C_t$). The parameters, $C_m$, $u$ and $V$ are known. This procedure, when applied to the analysis of Mg, Ni and even Cr of nonlinear working curve, offered a precision of about 0.7 percent. The procedure has the merit of not presuming linearity of the calibration curve. The exact location of the true zero-time on the recorded absorbance profile, however, could be imprecise for the curve may fail to take off sharply from the time axis.

Tyson et al.\textsuperscript{45,46} injected standards in turn into a sample carrier stream. This generated positive and negative peaks (depending on whether standard concentrations are greater or smaller than sample concentration). The algebraic difference of the absorbances, $\Delta A$, was plotted against the concentration of standards and the point at which the curve cut the concentration axis gave the concentration of the sample. This is a standard additions method and it was used to analyse Cr in steel with a precision of less than 0.1 percent. The procedure has the advantage of not presuming a linear curve output. A variant of the procedure, involving the injection of only one standard and a blank, has been reported and adapted for calibrations in ICP-AES by Israel and Barnes.\textsuperscript{126} Fang et al.\textsuperscript{125} reported another variant of the standard addition procedure for flame atomic emission spectrometry. This method is depicted in Fig. 1.6. The method (termed gradient standard addition) has a flow configuration such that water flows to the detector during the filling of the sample loop and the standard solution flows upon
Fig. 1.6. Calibration by standard additions using flow injection zone penetration method.

(I), manifold configuration. (II), Intensity-time profiles for the injected sample; and standard solution; in water stream. (III), intensity-time profile for the sample zone dispersed into water (leading edge) and standard solution (tail).

S, sample; C, standard solution; V, slider valve; W, waste; P, peristaltic pump; T, timer; FAES, flame atomic emission spectrometer; R, recorder; I, injection; and D, dispersion coefficient which is identical at the times $t_s$ and $t_s+c$ so that peak heights, $H_s$ and $H_s+c$, could be quantitatively related to the concentration of standard.

injection. This permits the injection plug of the sample (or blank) to be propelled into the carrier stream of the standard solution with water preceding the sample zone. The standard solution gradually dispersed into the sample zone and the signal profile was recorded. An equation derived from the dispersion coefficient and intensity peak heights was used to calculate the concentration of the sample. The procedure
was used to analyse soil extracts for Ca with a precision of 0.03 percent at 47 mg l\(^{-1}\). The authors applied this procedure in conjunction with wavelength scanning of the analyte. Hence, the procedure required an electronic injection device and a fast data acquisition accessory to offer precise results. The standard addition procedure reported by Araujo et al.\(^{127}\) is based on a similar principle. The workers, however, generated the concentration gradients for the standard solution separately, by its injection into a water carrier stream. The standard was then merged with a continuous flow of the sample (or water-blank for the calculation of dispersion coefficients). The signal heights (that have identical dispersion coefficients) at fixed time intervals on the recorded profiles were the data used for the calculation of the sample concentration. This procedure was effected without electronic timing and hence appeared easier to operate than the zone sampling-merged zone technique, originally reported by Gine et al.\(^{128}\) The former, however, has the demerit of a higher sample consumption. All these procedures, used for standard additions in FIA, have the limitation of assuming a constant interference factor and with the exception of references 45 and 46 have the limitation of assuming a linear calibration graph for the analyte. The latter limitation also applies to the network manifold of Tyson and Bysouth\(^{53}\) in which a single standard, injected into a carrier stream, is split into two or more streams and later made partially to overlap down stream. This generated a response profile of peaks and troughs. The dilutions at the peaks and troughs are accurately known and the manifold was applied to the analysis of Mg in the calibration range of 0.2 - 100 mg l\(^{-1}\) with a precision of 2 percent.

Tyson and coworkers\(^{48,102}\) were able to extend calibrations to higher concentrations, that normally would give off-scale absorbance, by using peak width data acquisition instead of peak height. The method, although it had poor precision, could be used to screen samples with off-range signals and so obtain the appropriate dilution factors for an accurate analysis. Concentrations of up to 1000 mg l\(^{-1}\) Mg were determined using the procedure. In addition, the authors also reported two other manifolds which were used for conducting an automated on-line dilution of standards by matching flow rates as well as generating variable dispersions from different dimensions of tubes. The former manifold offered recalibrations by the null measurement method\(^5\) whilst the latter offered a fast but less precise calibration using a single standard\(^{52}\).

A manifold that offers a dilution factor of up to 500 was recently reported by Whitman and Christian.\(^{129}\) The manifold design incorporates a splitting and merging streams combination that requires flow through pumps at the "analytical"
arms of the splits to maintain a reproducible flow rate ratio. Though the manifold was applied to the determination of chlorides by solution spectrophotometry, the high dilution factor as well as the reported advantage over zone sampling (absence of precision timing or computer controlled valves) can be similarly useful in FI-flame AAS. In summary, the literature reports of the dilution capabilities of different manifold features are shown, for easy comparison, in Table 1.2.

Table 1.2. Typical literature reports of possible on-line dilutions

<table>
<thead>
<tr>
<th>manifold feature</th>
<th>maximum dilution factor obtainable</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>mixing chamber</td>
<td>14</td>
<td>50, 124</td>
</tr>
<tr>
<td>network</td>
<td>28</td>
<td>53</td>
</tr>
<tr>
<td>variable tube dispersions</td>
<td>40</td>
<td>52</td>
</tr>
<tr>
<td>merging zones</td>
<td>40</td>
<td>33</td>
</tr>
<tr>
<td>time based micro-volume injections</td>
<td>80</td>
<td>56</td>
</tr>
<tr>
<td>zone sampling</td>
<td>130 - 10^3</td>
<td>122</td>
</tr>
<tr>
<td>splitting-merging streams</td>
<td>500</td>
<td>129</td>
</tr>
</tbody>
</table>

The very high dilution factors, in the range $10^3$ - $10^6$, were the results of the ingenious combination of two or more of these features which were effected with accurate timing and computer control.\textsuperscript{130,131}

1.3.3. Preconcentration and matrix modification

The procedures that are used for matrix modification or sample clean-up also show the capability to preconcentrate the analyte in FI-AAS. This usually occurs when the analyte is isolated from the sample matrix with the result that the power of detection (or sensitivity) is enhanced. The manifold designs are such that the separation techniques involving gas-liquid (gas diffusion and hydride generation), liquid-liquid (extraction) and liquid-solid (ion-exchange, adsorption, precipitation, dissolution and stripping) are performed reproducibly in continuous modes even if the reaction
changes have not attained equilibrium. Subsequently, indirect analysis of anions or organic groups, speciation studies and analysis of real samples are now performed with relative ease and at higher sample throughput than in the conventional flame AAS methods. Manifolds incorporating liquid-liquid extraction chambers, ion-exchange minicolumns and gas separators have undergone fast developments and are now available in dedicated commercial instruments. However, the incorporation of solid-liquid filtration units and electrochemical flow-through cells are recent developments in FI-AAS.

Nord and Karlberg were first to describe a manifold incorporating liquid-liquid extraction which improved analytical sensitivity in the direct determination of metal ions in aqueous samples. The extractant reagent used was ammonium pyrrolidine-dithiocarbamate (APDC) in IBMK. Using a similar manifold, Sweileh and Cantwell determined Zn in a solution containing a large excess of iron interferent (having a spectral overlap at 214 nm). The sample, with ascorbic acid/thiocyanate reagent, was segmented with IBMK and the analyte finally extracted as the Zn(SCN)$_2^{++}$ complex into IBMK and detected. The manifold had a T-piece solvent segmentor and a porous teflon membrane phase separator. The extracting solvent, IBMK, was pumped at low flow rate and introduced continuously into the nebuliser, as in Fig. 1.3(v). The same solvent was used to compensate the nebuliser flow rate. The authors reported that air compensation caused water to break into the organic phase and, hence, offered poor precision. Water compensation, on the other hand, offered low sensitivity. With improvement in the manifold design such that the extraction unit is put before an injection system, Silva et al. carried out an indirect determination of nitrate and nitrite mixtures. A carrier solution of Cu$^{++}$/hydroxylammonium sulphate/PO$_4^{3-}$ with the sample was merged with a stream of neocuproine in IBMK. The extracted neocuproine/copper(I) chelate, ionpaired with the nitrate, was injected into a water carrier stream and detected by flame AAS as in Fig. 1.3(vi). When cerium(IV) was added to the sample, the absorbance was proportional to both the nitrate and nitrite concentration, and when sulfamic acid was added to the sample, the absorbance was proportional to the nitrate concentration alone. Meat and vegetable products were analysed and the nitrate and nitrite ions were extracted with 98-102 percent recovery. As low as 0.5 mg l$^{-1}$ of each anion was conveniently determined.

The developments in manifold design aimed at replacing the segmentor, extractor coil and phase separator with simpler devices. There are reports of
liquid-liquid extractions conducted without liquid segmentation and phase separations. Such extractions depend on the fabrication of suitable extraction cells and flow configurations. Thus, Sahlestrom and Karlberg\textsuperscript{138} devised an extraction cell which had two grooves (one for sample carrier and the other for the extracting solvent) separated by a PTFE membrane; Adunsson\textsuperscript{139} devised a similar extraction cell but with a liquid membrane (prepared as a PTFE membrane soaked in a solvent); and Canete et al.\textsuperscript{140} used flow reversals in the loop of the injection valve that contained the detector to avoid liquid segmentation and phase separation. Whilst these improvements are reported for solution spectrophotometry, some which effected the liquid-liquid extraction via a "solid intermediator", such as reported by Karlberg, could be useful in FI-AAS\textsuperscript{136(a)}. The "solid intermediator" was a reversed-phase octadecylsilane bonded silica gel packed in a minicolumn. The column material trapped neutral caffeine molecules from aqueous carrier which was later eluted with methanol. The extraction was effected using a miscible solvent in a simple manifold similar to that used for ion exchange procedure in FI-flame AAS (see Fig. 1.3(vii)). The recent report of Ruzicka and Arndal on sorbent extractions in FI-flame AAS,\textsuperscript{136(b)} showed an extensive application of the "solid intermediator" principle. The chelated complexes of Cu and Pb with diethyldithiocarbamate (formed as the sample in a carrier stream, merged with the reagent) were sorbed on octadecylsilane bonded silica gel packed in a minicolumn. Methanol was used to elute the complexes and the manifold was similar to that shown in Fig. 1.3(vii).

The improvement\textsuperscript{136(b)} overcome the drawback of the phase separator. The aqueous or organic phase being separated may penetrate each other especially at high pumping flow rates. The effect is pronounced in FI-flame AAS if the optimum liquid uptake of the nebuliser is not compensated.\textsuperscript{54} At present, the manifold configuration shown in Fig. 1.3(vi), that puts the extraction unit prior to an injection system, has preference over Fig. 1.3(v). This manifold offers intermittent nebuliser wash periods which overcome the disadvantage of continuously streaming the organic phase to the nebuliser.

 Ion-exchange _ Olsen et al.\textsuperscript{103} first described a single channel manifold that incorporates an ion-exchange microcolumn of 2 mm internal diameter and 50 mm long. The column was packed with an iminodiacetate chelating resin (chelex-100 exchanger) and was used to preconcentrate \( \mu \)g l\(^{-1}\) amounts of Cu, Zn, Pb and Cd from sea water. The ions were eluted with pulses of dilute acid to the nebuliser. Columns and manifolds have undergone much improvement so that concentration
I efficiencies (the product of the enrichment factor and the sampling frequency) of 50-100 fold min\(^{-1}\) are readily attained. This makes flame FI-AAS of comparable sensitivity to graphite furnace AAS (GF-AAS) and it also has an edge over GF-AAS by achieving a 2-3 fold sample throughput as well as separating analyte from most matrix elements. Presently, the only demerit of flame FI-AAS is the relatively large sample volume consumed in order to offer an equivalent sensitivity as GF-AAS. The proposed solution to overcome this demerit lies in the design of nebulisers and spray chambers specifically for FIA.

Malamas et al. used a silica-immobilised 8-quinolinol (SHQ) chelating exchanger on a porous glass support to preconcentrate transition metal ions from sea water. This procedure offered an enrichment of about 250-fold. The alkaline earths (Ca and Mg) as well as Al, however, could only be retained at high pH or when the ion-exchange capacity was large. Allen et al. succeeded in using EDTA immobilised on porous glass to preconcentrate Al from aqueous solutions and Garcia et al. used a strongly basic anion-exchange resin, Amberlite IRA-400, to preconcentrate Al from aqueous solutions and haemodialysis fluids. In the latter report, the buffer component, 2-(N-morpholino) ethane sulphonic acid, aided the exchange phenomenon though serum Al, without acid digestion, could not be exchanged by the system. Marshall and Mottola described a relatively simple manifold with a column packed with SHQ (amino-phenyl immobilised) on a low cost silica gel support. This manifold afforded a detection limit of 1.5 \(\mu\)g l\(^{-1}\) for Cu in water samples. The recent introduction of adsorptive alumina as a column material gave the simplest manifold operation and lowest cost compared to the other columns. This column is more versatile for it can retain both anions and cations with proper adjustment of pH. Although the manifold was originally reported for ICP-AES, it has been applied in flame AAS for the analysis of Pb, an element which does not suffer from aluminium interference.

Improvements in the manifold design, used for ion exchange separations, have aimed at effecting a homogeneous mixing of sample and buffer so as to aid the efficient retention of ions on the column material. The minimisation of carryovers and changes in the compactness of the resin are also important (the earlier condition requires elution reactions to be quantitative). Therefore, the manifold configuration of a single channel had added onto it a merging stream as in Fig. 1.2(vii), then a counter-flow elution and finally a diversion of waste from the nebuliser with water flushing the nebuliser to prevent possible nebuliser blockage. A fully automated...
The practice of placing the minicolumn in the loop position of the injection system, as reported by Bysouth et al. and Fang et al., may not offer an improvement in sensitivity but does offer a less complex manifold. The incorporation of dual columns has offered increased sample throughput. In addition, the serial coupling of ion-exchange manifolds with hydride generation and cold vapour FI-AAS has offered improved concentration efficiencies and improved tolerance to interferences.

Hydride/vapour generations. The first manifold for hydride generations in FI-AAS was reported by Astrom. The author merged a carrier stream of 1.2 M HCl with a stream of 1 percent sodium borohydride in 0.1 M NaOH. This solution was sprayed, on-line, with nitrogen (or argon) into a Vijan-type U-tube gas-liquid separator. The gaseous hydride was swept into a quartz tube for AAS detection. A solution of 30 µg l⁻¹ Bi was analysed with a precision of less than 1 percent and a sampling rate of 180 h⁻¹. The detection limit was 0.08 µg l⁻¹ (at a signal to noise ratio, SNR, of 3). The matrix interferences which are normally associated with hydride gas generations were substantially reduced because this FI-method offered a reduction in reaction time. The sensitivity obtained, however, was low in comparison with air-segmented systems. In a later report, Fang et al. miniaturised the U-tube phase separator to a small bulb of 15 mm i.d. This offered improved sensitivity compared to the bigger separator when the manifold was applied to the determination of selenium, arsenic and lead. De-Andrade et al. applied the FI-hydride generation system to the cold vapour determination of mercury. Their manifold incorporated a special vapour-diffusion cell which had a phase separator combined with an absorption cell. The phase separation was effected through a PTFE membrane of about 2 mm thickness. This manifold offered a detection limit of 0.66 µg l⁻¹ Hg (at an SNR of 2) and a precision of 1% RSD with a sampling rate of 110 h⁻¹. A thinner membrane of thickness 0.075 mm was backed with a nylon gauze for mechanical strength and used in a similar vapour-diffusion cell by Fang et al. This improved detection limit to 0.06 µg l⁻¹ Hg (at an SNR of 3) compared with thick membrane. Also, a precision of 1% RSD at 4 µg l⁻¹ and a sample throughput of 200 h⁻¹ were realised. Although the vapour diffusion cell has been miniaturised so as to increase the atom population in the absorption cell, the reported sensitivity and sample throughput, however, are still of the same order as for cold vapour AAS using a U-tube phase separator. Moreover, a detection limit of 1 ng l⁻¹ Hg, reported by Hawley and Ingle, for their conventional gas carrier flow system, is yet to be attained. A recent report, by
Bimie,\textsuperscript{153} of a manifold which incorporated a modified U-tube gas-liquid separator prior to a silica absorption cell offered poor response characteristics in comparison with those of the vapour-diffusion cell. Thus, the detection limit was 20 mg l\textsuperscript{-1} with a sampling rate of 20 h\textsuperscript{-1}. However, the sample digestion could be carried out on-line. In addition, the manifold could offer a speciation determination of both organic and inorganic mercury in natural and waste waters, provided the samples do not contain interferents such as sulphide and chloride ions.

Using a system based on the manifold of Astrom, Yamamoto et al.\textsuperscript{154} determined \(\mu g\) l\textsuperscript{-1} amounts of As, Sb, Bi, Se and Te to a detection limit of 0.04 - 0.3 ng (at an SNR of 3) in 0.5 ml of samples. The precision was less than 2.5\% RSD with a sample throughput of 120 h\textsuperscript{-1}. A selective determination of As(III) in the presence of As(V) and of Sb(III) in the presence of Sb(V) was effected with a suitable adjustment of pH in the manifold. These workers used air-segmentation of the carrier stream to improve the peak height sensitivity of the absorbances obtained. Pacey et al.\textsuperscript{155} incorporated a dual phase gas-diffusion cell before the spectrometer in a similar manifold. This cell offered the diffusion of gaseous products through a PTFE membrane (0.45 \(\mu m\) pore and supported on the gas stream side with a nylon mesh) into a gas phase that streamed to a "flame in a tube"\textsuperscript{156} quartz atomisation cell. With the exception of Se, the manifold offered an improved selectivity of separating both As(III) and Sb(III) from their higher oxidation state species. The detection limit of 10 \(\mu g\) l\textsuperscript{-1} (at an SNR of 3), was claimed to be a hundred times improvement over the U-tube gas-liquid separator, at a precision of less than 1\% RSD in the linear range of 10 - 160 \(\mu g\) l\textsuperscript{-1} and a sample throughput of 180 h\textsuperscript{-1}. The gas diffusion cell used by Yamamoto et al.\textsuperscript{157} had a microporous teflon tube (Gore-Tex tube 3 mm i.d., 4 mm o.d. and 70\% porosity) membrane separator as the inner tube of a Pyrex glass tube (8 mm i.d.). This tube membrane provided a large surface area for the gas diffusion and when applied to the determination of As in surface waters, it offered a precision of 2.5\% RSD, in the concentration range of 1.3 - 3.5 \(\mu g\) l\textsuperscript{-1}, with a sample throughput of 150 h\textsuperscript{-1}. There was, however, no report on the detection limit apart from the fact that this tube membrane offered a decreased interference from foreign ions compared with a U-tube separator.

Tyson et al.\textsuperscript{43} used the type of teflon tube membrane of Yamamoto et al.\textsuperscript{158} to separate copper trifluoroacetylacetonate. The complex was solvent extracted, vaporised in a heated oven and introduced into the burner of a flame atomic absorption spectrometer. The procedure, still at its preliminary stages, offers a new
trend in vapour generation FI-flame AAS. That is, a volatile derivative could be solvent extracted from an interfering matrix and fed as the vapour to spectrometer with the flame as the absorption cell. This procedure may offer an improved sensitivity similar to conventional hydride/vapour generation AAS. However, the improvement may be subject to the device of an efficient manifold-nebuliser interfacing.

At present, an improved detection limit for hydride generation FI-AAS, similar to those of conventional methods, is realised by incorporating ion-exchange minicolumns at the start of the manifolds. However, sample throughput is decreased. Using a minicolumn of chelating resin with iminodiacetate group, ng amounts of Se in metal alloys were determined to a detection limit of 0.1 ng with a precision of 3.8% RSD at 30 h⁻¹. Microporous strongly basic anion-exchanger improved the detection limit of Se to 2 ng l⁻¹ at 50 h⁻¹ and quinolin-8-ol treated controlled pore glass column (CPG) also offered a detection limit of 2 ng l⁻¹ for Hg at 60 h⁻¹. Nakata et al. envisaged that an improvement in sensitivity, without a loss in sample throughput, could be offered by the ICP-AES detector due to its high atomisation temperature. However, their report showed that an element such as Ge had its detection limit not much better than using atomic absorption detection.

Precipitations_ Martinez-Jimenez et al. incorporated a stainless steel membrane filter of 0.5 μm pore diameter and 3 cm² filter area into manifolds which were devised for precipitation reactions in FIA. The generated precipitates were either continuously retained, thereby recording depressions in the monitored absorbance, or subsequently dissolved to obtain absorbance peaks in FI-flame AAS. The filter was mounted in a HPLC solvent cleaning microcolumn. The manifolds were applied to determine chloride content of different water samples, in a range of 3 - 100 mg l⁻¹ with 2% RSD at a sampling rate of 50 h⁻¹ for a normal flow FIA, and a range of 0.3 - 10 mg l⁻¹ with 4% RSD at 200 h⁻¹ for a reversed flow FIA. Further application of the manifolds was in the determination of the chloride and iodide contents of foodstuffs and wines. The concentration of chloride and iodide (mg l⁻¹ amounts) in the ratios that ranged from 8 : 1 to 1 : 60 were determined with a sampling rate of 10 h⁻¹. The absorbance of the reagent, AgNO₃, was monitored as base line and the precipitates formed (retained on the filter) when the reagent and the sample were merged caused a depressive FI-peak which was proportional to the concentrations of both chloride and iodide. A stream of 6 M NH₃ was used selectively to dissolve AgCl which caused a positive FI-peak. This peak height was proportional to the concentration of chloride. The
concentration of iodide was calculated by difference. The authors also reported the application of the manifolds to preconcentrate Pb as the hydroxide (Pb\(^{2+}/\text{NH}_3(\text{aq})\) reaction).\(^{67}\) In this case, the precipitates were eluted with HNO\(_3\) and Pb was determined in the range of 1.2 - 1500 mg l\(^{-1}\). The detection limit was 20 \(\mu\)g l\(^{-1}\) with 1% RSD at a throughput of 15 h\(^{-1}\). This detection limit was reportedly lowered to 1 \(\mu\)g l\(^{-1}\) with 4% RSD at 1 h\(^{-1}\). Santelli et al.\(^{62}\) carried out further adjustments in the earlier manifolds\(^{63,160}\) such that the precipitation effluents are diverted off the nebuliser. Water washed the nebuliser, in the interim, by suction. The adjusted manifold was used to determine \(\mu\)g l\(^{-1}\) concentrations of Cu in silicate rocks. Cu(II)/dithiooxamide precipitation reaction was used and this permitted the determination of Cu with 1% RSD at a sampling rate of 20 h\(^{-1}\). The detection limit of 5 \(\mu\)g l\(^{-1}\) was improved to 0.3 \(\mu\)g l\(^{-1}\) through preconcentration by a factor of 500. This, however, lowered the sample throughput to 1 h\(^{-1}\).

Adeeyinwo and Tyson devised a precipitation manifold to increase the tolerance of aluminium in the determination of Ca in flame AAS.\(^{163}\) Ammonia/ammonium oxalate solution was the reagent used to precipitate the Ca. The eluting solvent was HCl. Up to 200 mg l\(^{-1}\) aluminium in 10 mg l\(^{-1}\) Ca was removed with a precision of 2% RSD and a sampling rate of 12 h\(^{-1}\). Different filtration units such as column of inert materials of glass beads or polystyrene granules, which in some experiments were combined with polymeric filter membranes, were studied.\(^{164}\)

**Electrodeposition**_ The incorporation of a flow-through electrochemical cell into a manifold for the determination of Pb in drinking waters was reported by Schulze et al.\(^{76}\) A potentiometric stripping analysis in serial coupling to flame AAS was the detection system. The flow cell, consisting of channels drilled into a Plexiglas cylinder, had a cartridge of carbon felt in one of its channels as working electrode. This electrode offered a 24% deposition efficiency of Pb with an enrichment factor of 5 at a sampling rate of 60 h\(^{-1}\). Multiple injections improved the enrichment factor to 30 at 12 h\(^{-1}\). A similar flow-through cell with a cartridge of reticulated vitreous carbon (RVC) as working electrode was sealed into a heat shrink PTFE body.\(^{165}\) The cell was used as a sampling device for the determination of Cu, Pb and Hg content of industrial waste waters. Deposition efficiencies in the range of 80 - 110% for RVC of 100% porosity were reported at \(\mu\)g l\(^{-1}\) concentrations of the analytes. The analytical measurements were made using in-line potentiometric stripping analysis and certified by off-line AAS. On-line electrolytic dissolution of steel was configured by Bergamin et al.\(^{166,167}\) A polished steel sample was made part of an
anode and fitted into one of the channels drilled into a teflon block which constituted the flow-through electrolytic cell. The steel sample was dissolved on application of current pulses. Aluminium was dissolved out of the steel in a stream of an acidified solution of KCl and transported along the flow line for further analytical reactions needed for a spectrophotometric detection. The manifold permitted the determination of Al in "killed" steel in the range of 0.01 - 0.13% (m/m) with a sampling rate of 20 - 40 h\(^{-1}\). This report, however, was silent on the precision of the method. This manifold was later applied to determine molybdenum in steel\(^{168}\) with a linear range of 0.7 - 2.7% (m/m). The precision was 2.3% RSD at 2.21% (m/m) Mo at a sampling rate of 40 h\(^{-1}\). Such special flow cells have been interfaced with ICP-AES\(^{169}\) and applied to determine Al in steel and other ferrous alloys with a sample throughput of 60 h\(^{-1}\). It has been proposed that such flow cells, also, be interfaced with AAS to determine Al\(^{170}\).

1.3.4. Indirect analysis

Indirect analysis in AAS involves the determination of nonmetals, anions or organics\(^{171,172}\). Analyses have been carried out using appropriate reactions with or without phase separations. The following methods have been typical: chemical interference of the analyte on a metal ion in the flame; solvent extraction or masking the extraction of an equivalent amount of metal; oxidation or reduction of a metal by the analyte followed by solvent extraction; and partial precipitation of a metal ion by the analyte in a solution of excess metal ion. In all cases, it is the suitable metal that is detected by AAS and the analyte concentration deduced from it. With the advent of FI-AAS, all these time consuming procedures can now be carried out subject to the devising of appropriate manifolds\(^{11,173}\).

Haj-Hussein et al.\(^{69}\) packed a minicolumn with cupric sulphide and incorporated it into a single line manifold, for cyanide analysis. The soluble cuprocyanide complex released on injection of aqueous cyanide samples into a KOH (pH 11) carrier stream, was nebulised for Cu measurement. This permitted the indirect analysis of cyanide with 2% RSD at 26 mg l\(^{-1}\) with a sampling rate of 45 h\(^{-1}\). The detection limit was 1 mg l\(^{-1}\) and the presence of up to 20-fold of anions such as acetate and halide (except citrate) did not interfere with the analysis.

The use of a solvent extraction manifold to determine nitrate and nitrite in meat and vegetables, as reported by Silva et al.\(^{135}\), has been discussed in section 1.4.3. Earlier, Gallego and Valcarcel\(^{68}\) determined perchlorate in urine and serum using a
solvent extraction manifold. The reagent, 6-methylpicoline aldehyde azine (6-Me-PAA) dissolved in IBMK, was used to extract the continuously pumped perchlorate sample which had been merged with a stream of copper(II) solution. The copper complex was nebulised and this permitted the determination of perchlorate in the range of 0.1 - 5.0 mg l\(^{-1}\). The precision of the determination, however, was not indicated. Several anions, except EDTA and thiocyanate, did not interfere in the analysis.

The researches of Valcarcel and coworkers on the analytical application of precipitation manifolds in flame FI-AAS have dealt with the indirect determination of inorganic anions such as Cl\(^{-}\), I\(^{-}\) and oxalate.\(^63,160,161\) The analytical characteristics of the methods have been summarised in section 1.3.3. The latest application of their manifold is in the analysis of local anaesthetics in pharmaceutical preparations.\(^174\) Lidocaine, procaine and tetracaine (all organic compounds) were determined at mg l\(^{-1}\) concentrations, in a linear range of 2.5 - 35.0 mg l\(^{-1}\), by their precipitation with cobalt(II). These drugs were analysed using the reversed FIA procedure. In this procedure, microliter volumes of cobalt(II) were injected into a water stream and the absorbance was recorded by flame AAS. The same aliquots were injected into the sample stream to give reduced absorbances. The difference in absorbances, in both water and sample carriers, was proportional to the concentration of the organic analyte. The problem of continuous retention of the precipitates, that could cause a variation in flow rates and hence lead to errors in the results, was minimised by the frequent washings of the filter unit in an ultrasonic bath. The manifold offered a 1% RSD at 10 mg l\(^{-1}\) and a linear range of 2.5 - 35 mg l\(^{-1}\) of the analyte with a throughput of 100 h\(^{-1}\).

1.3.5. Multicomponent/Speciation analysis

This procedure involves analytical measurements of the different elements (multicomponent) or different oxidation states of an element (speciation). The measurements are preferably made from a single aliquot of the sample in a single run.

Lynch et al.\(^74\) were first to carry out speciation studies by FI-AAS. They determined Fe in mineral process solutions and Cr in corrosion testings and sea water. Their manifold had the outlet of a visible spectrophotometer connected to a flame AA spectrometer in a serial coupling. The AA spectrometer determined the total element whereas the visible spectrophotometer determined the coloured product.
of Fe(II) or Cr(VI). Burguera and Burguera\textsuperscript{75} at about the same time, used a similar manifold arrangement to determine Fe(II) and total Fe in polluted waters. The expense of a multidetector system was later avoided with the use of on-line ion-exchange columns. Thus, Milosavljevic et al.\textsuperscript{175} incorporated an ion-exchange column of chelating resin with salicyclic acid functional group in a single line manifold to determine copper species. The sample, a mixture of Cu\textsuperscript{2+} and [CuEDTA]\textsuperscript{2-}, was injected into a water carrier stream through the column to a flame AA spectrometer. The complexed Cu gave signal whilst the free Cu\textsuperscript{2+} was retained to be eluted with the injection of 2 M HNO\textsubscript{3}. The manifold offered a 2% RSD at 0.5 mg l\textsuperscript{-1} for the complexed Cu and 1% RSD at 0.2 mg l\textsuperscript{-1} for the free metal ion. This manifold was further applied to the preconcentration of chromium in which the column retained cationic Cr(III) whilst anionic Cr(VI) passed through to the flame AA spectrometer.\textsuperscript{176} Subsequent elution of the column with 2 M HNO\textsubscript{3} offered the determination of Cr(III) at sub-microgram concentrations with a sampling rate of 60 h\textsuperscript{-1}. The unretained Cr(VI) was determined at lower milligram concentrations. Precision for each ion was less than 1% RSD and detection limits for the retained and unretained ions were 16 µg l\textsuperscript{-1} and 85 µg l\textsuperscript{-1} respectively. Liu and Ingle\textsuperscript{177} incorporated two columns of different ion-exchange materials in a sequence to a flame AA spectrometer. Each column retained a different species of the injected metal ion and elution at different times gave the retained species. Two fractions of the species of Cu(II), Cd(II) and Zn(II) in natural waters were determined at 0.1 µg l\textsuperscript{-1} concentrations with an enrichment factor of 50 and a sample throughput of 6 h\textsuperscript{-1}. This manifold had the additional benefit of being automated. The manifold reported by Patel et al.\textsuperscript{178}, however, had a single column of silica bonded strong anion exchanger for the preconcentration and speciation of vanadium. The sample, adjusted to pH 2.5, was pumped into a 0.01 M HCl carrier stream. The species, V\textsuperscript{V}, was retained whilst V\textsuperscript{IV} passed through to the N\textsubscript{2}O-C\textsubscript{2}H\textsubscript{2} flame AA spectrometer. The V\textsuperscript{V} was eluted with 0.5 M NaOH and determined with a precision of 3% RSD at 50 µg l\textsuperscript{-1}. A sampling rate in the range 60 - 240 h\textsuperscript{-1}, that was reported, was dependent on the sample volume. The linear range was 0.2 - 1 mg l\textsuperscript{-1}.

Silva et al.\textsuperscript{135} successfully determined the nitrate and nitrite in food samples using a solvent extraction manifold as described in section 1.3.3. The manifold, however, was more complicated than that used for ion-exchange. Also, Martinez-Jimenez et al.\textsuperscript{161} used a precipitation manifold to determine the halide components of a mixture. This has been described in section 1.3.3. The use of a
manifold that incorporated an adsorptive alumina minicolumn to determine Cr(VI) and Cr(III), by ICP-AES, has been reported by Cox and McLeod. The column, however, is yet to be applied in FI-AAS for multielement or speciation studies though it has been used for the preconcentration of Pb from drinking waters.

1.3.6. Real Sample Analysis

The application of FI-AAS to the determination of inorganic cations in clinical samples such as blood and environmental samples (especially water pollutants and soils) is well documented in text books and reviews. Amongst these publications, those authored by Tyson and Fang et al. are solely for applications in FI-AS. In these works, real sample analysis by flame FI-AAS was originally performed to increase the sample throughput of those samples that would normally clog the nebuliser capillary or extinguish the flame. The elimination of matrix effects, preconcentration of low levels of analyte and speciation studies are later developments, most of which have been discussed in section 1.3.3. A summarised survey of the flame FI-AAS determination of several elements in various real samples, in the period from early 1986 to early 1990, are presented in Table 1.3. There is a clear indication that the scope of flame FI-AAS has widened to cover the analysis of agricultural, food, pharmaceutical and metallurgical samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Analyte/metal determined</th>
<th>Manifold feature</th>
<th>Reference (year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLINICAL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Serum</td>
<td>Co, Mn</td>
<td>-</td>
<td>185 (1986)</td>
</tr>
<tr>
<td>3. Whole blood</td>
<td>Cu, Zn, Fe</td>
<td>on-line microwave oven</td>
<td>186 (1986)</td>
</tr>
<tr>
<td>4. Serum</td>
<td>K, Mg, Mn, Fe, Cu, Co, Zn, Ca</td>
<td>-</td>
<td>187 (1986)</td>
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</table>
Table 1.4. continued

<table>
<thead>
<tr>
<th></th>
<th>Sample Type</th>
<th>Elements</th>
<th>Method</th>
<th>Year</th>
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<tr>
<td>5.</td>
<td>Serum</td>
<td>Zn</td>
<td>-</td>
<td>6 (1986)</td>
</tr>
<tr>
<td>6.</td>
<td>Haemodialysis fluid</td>
<td>Al</td>
<td>ion-exchange, immobilised chromoazurol S</td>
<td>188 (1986)</td>
</tr>
<tr>
<td></td>
<td>and serum</td>
<td></td>
<td>anion exchange, Amberlite IRA-400</td>
<td>144 (1987)</td>
</tr>
<tr>
<td></td>
<td>and tap water</td>
<td></td>
<td>anion exchange, Amberlite IRA-400</td>
<td>189 (1986)</td>
</tr>
<tr>
<td>8.</td>
<td>Cerebrospinal fluid</td>
<td>Na, K, Ca, Mg, Fe, Cu, Zn</td>
<td>-</td>
<td>190 (1987)</td>
</tr>
<tr>
<td>12.</td>
<td>Urine</td>
<td>Pb</td>
<td>off-line solvent extraction, (APDC/IBMK)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.</td>
<td>waters</td>
<td>Ca, Mg, Na, K</td>
<td>-</td>
<td>206 (1989)</td>
</tr>
<tr>
<td>14.</td>
<td>waters (power station cooling circuits)</td>
<td>Cu</td>
<td>solvent extraction (APDC/IBMK)</td>
<td>207 (1989)</td>
</tr>
<tr>
<td>15.</td>
<td>Natural waters</td>
<td>Cu, Cd, Zn</td>
<td>ion-exchange, 2 columns of chelex 100 &amp; AG MP-1 in series</td>
<td>177 (1989)</td>
</tr>
<tr>
<td>16.</td>
<td>sea water</td>
<td>Cd, Cu, Pb</td>
<td>ion-exchange, CPG/quinolin-8-ol</td>
<td>208 (1989)</td>
</tr>
<tr>
<td>17.</td>
<td>tap water</td>
<td>Pb</td>
<td>ion-exchange, immobilised 2-methyl-8-quinolinol</td>
<td>149 (1988)</td>
</tr>
<tr>
<td>18.</td>
<td>drinking water</td>
<td>Pb</td>
<td>ion-exchange, activated alumina</td>
<td>148 (1988)</td>
</tr>
<tr>
<td>19.</td>
<td>drinking water</td>
<td>Pb</td>
<td>precipitation-dissolution</td>
<td>67 (1987)</td>
</tr>
<tr>
<td>20.</td>
<td>drinking water</td>
<td>Pb</td>
<td>electrodeposition</td>
<td>76 (1987)</td>
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<td>21.</td>
<td>wells, spring</td>
<td>Cl^-/Ag</td>
<td>continuous precipitation</td>
<td>160 (1987)</td>
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<td>22.</td>
<td>sea, tap, waste waters</td>
<td>Co</td>
<td>ion-exchange, (quinolin-8-ol CPG)</td>
<td>115 (1988)</td>
</tr>
<tr>
<td>23.</td>
<td>waters</td>
<td>Hg</td>
<td>cold vapour AAS, with ion-exchange, (8-quinolinol CPG)</td>
<td>194 (1988)</td>
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<tr>
<td>24.</td>
<td>waste waters</td>
<td>Hg</td>
<td>cold vapour AAS</td>
<td>153 (1988)</td>
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<tr>
<td>Table 1.4. continued</td>
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<tr>
<td>25. waste waters</td>
<td>anionic surfactants /Cu(II)</td>
<td>solvent extraction, (neocuproine/IBMK)</td>
<td>195 (1986)</td>
<td></td>
</tr>
<tr>
<td>26. sewage sludge</td>
<td>Cu, Mn</td>
<td>-</td>
<td>209 (1989)</td>
<td></td>
</tr>
<tr>
<td>27. soils and plants</td>
<td>As</td>
<td>hydride generation AAS</td>
<td>196 (1988)</td>
<td></td>
</tr>
<tr>
<td>28. soils and plants</td>
<td>Hg</td>
<td>cold vapour AAS</td>
<td>197 (1987)</td>
<td></td>
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<tr>
<td>29. silicate rock digest</td>
<td>Co</td>
<td>precipitation-dissolution</td>
<td>214 (1989)</td>
<td></td>
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<tr>
<td>30. silicate rock digest</td>
<td>Cu(II)</td>
<td>precipitation-dissolution</td>
<td>162 (1989)</td>
<td></td>
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<tr>
<td>31. silicate rock digest</td>
<td>Mg</td>
<td>-</td>
<td>198 (1986)</td>
<td></td>
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<tr>
<td>32. silicate rock leachate</td>
<td>Na, K</td>
<td>simultaneous determination, AAS-AAS dual detection</td>
<td>199 (1987)</td>
<td></td>
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<tr>
<td>33. silicate rock digest</td>
<td>Ca</td>
<td>-</td>
<td>200 (1986)</td>
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**FOOD**

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<tr>
<th></th>
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<th>Precipitation-dissolution, sequential determination</th>
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<tr>
<td>34. foodstuff</td>
<td>Cl⁻, I⁻/Ag</td>
<td>161 (1987)</td>
</tr>
<tr>
<td>35. foodstuff</td>
<td>Pb, Cd</td>
<td>201 (1987)</td>
</tr>
<tr>
<td>36. foodstuff</td>
<td>NO₂⁻, NO₃⁻ /Cu(I)</td>
<td>135 (1986)</td>
</tr>
<tr>
<td>37. foodstuff</td>
<td>Fe, Cu</td>
<td>Off-line microwave digestion</td>
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**METALLURGY**

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<tr>
<td>38. alloys</td>
<td>Cu, Pb</td>
<td>210 (1989)</td>
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<tr>
<td>39. tool steel</td>
<td>Co</td>
<td>solvent extraction</td>
</tr>
<tr>
<td>40. steel</td>
<td>Cr</td>
<td>-</td>
</tr>
<tr>
<td>41. galvanising solutions</td>
<td>Zn</td>
<td>in-stream sample filtration</td>
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**PETROLEUM**

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<table>
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<tbody>
<tr>
<td>42. gasoline</td>
<td>Pb</td>
<td>-</td>
</tr>
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</table>
Table 1.4. continued

PHARMACEUTICALS

43. sulphonamide drugs       bronquimucil, continuous precipitation       204 (1988)
    sulphintestin,
    oculos/ Cu ++(or Ag +)

44. anaesthetics              lido-, pro-, and continuous precipitation 174 (1988)
    tetra- caine
    hydrochlorides /Co(II)

HIGH-PURITY CHEMICALS

45. water                     Cu                                   ion-exchange 212 (1989)
46. standard                  Cd, Cu                                ion-exchange, Muromac A-1 213 (1989)

reference materials

1.4. FI-AAS CONTROVERSIES/AIMS OF RESEARCH

The development of FI-flame AAS has reached a stage at which all conventional methods of analysis can be performed rapidly with the following advantages: little or no contamination of the sample; low reagent and sample consumption; considerable tolerance to a high solute content of sample; and reduced interferences especially transport interferences arising from the viscosity changes of the sample. However, FI-flame AAS has an inherently poor signal to noise ratio because of the small (microliter) injected sample volumes. This intrinsic property of FI-flame AAS has generated some conflicting observations on the performance of the technique as to its ability to achieve the sensitivity, precision and detection limits similar to those obtained by conventional flame AAS.97

The parameters that affect sensitivity, precision and detection limits in FI-flame AAS are largely the flow rate of the carrier stream, the volume of the injected sample and the aspiration flow rate of the nebuliser.40 Wolf and Stewart34 showed that
decreasing the flow rate of the carrier stream increased nebulisation efficiencies such that peak area quantifications of copper and zinc offered better detection limits than the conventional aspiration sampling. Thus, the absolute detection limits of 4 ng Cu and 3 ng Zn are better than the values, of 50 ng Cu and 10 ng Zn, obtained by conventional aspiration. The workers stated that such improvements could not be obtained if the nebuliser liquid uptake was conventionally reduced. Their studies also showed that peak area precision (2.7% RSD) was invariant at low carrier flows of 1 - 4 ml min⁻¹ whereas peak height precision worsened (from 1.7% to 5.3% RSD) as the sensitivity decreased. Hamly and Beecher, from the same laboratory as Wolf and Stewart, used a similar FI- system to study Cu but had a contrary report. The workers reported improvements on the detection limits of both FI-peak area and FI-peak height quantifications as the injected sample volume increased. The detection limits were, however, not better than those of conventional aspiration.

Brown and Ruzicka on the other hand, reported an improvement in precision for the peak height quantification of Cu over that of conventional aspiration. The value of 0.44% RSD, with 150 µl injections, was significantly better than the 0.78% obtained for conventional aspiration. This occurred when the nebuliser liquid uptake and the FI- pumping flow rates were set equal, at 4.9 ml min⁻¹. The precision of FI-peak heights, however, became worse as the carrier flow rates decreased, an effect which was more pronounced for peristaltic pumping than gas pressurised pumping. In addition, the workers reported FI- flame AAS as having better peak height sensitivities than conventional aspiration. This effect occurred when nebuliser liquid uptake was 5 ml min⁻¹ or less and FI- pumping rate was 5 - 6 ml min⁻¹ or more (operation of the nebuliser at "flooded" flow). Therefore, the sample-conversion treatments in FI- flame AAS which require low carrier flow rates for optimum chemistries would be attended with improved nebulisation efficiencies but would have poor precision and reduced peak height sensitivity.

Garcia et al. applied an air bleed close to the nebuliser in the FI- flame AAS of calcium. The authors reported that a nebuliser operated at maximum negative pressure with air compensation permitted FIA sensitivities to be equal to or better than those of conventional aspirations at low carrier flow rates of 0.4-3.8 ml min⁻¹. The detection limits of 0.018 and 0.019 µg l⁻¹ for peak area and peak height quantifications (60 µl injections of 4 µg Ca at 1.8 ml min⁻¹), however, are not significantly different from the value of 0.020 µg l⁻¹ obtained by conventional aspiration. Sweileh and Cantwell, on the contrary, reported a variable baseline
and poor reproducibility of signals when air compensation was applied in the
determination of Zn by liquid-liquid extraction in FI- flame AAS. In addition, the
workers\textsuperscript{54} reported that the operation of the nebuliser at "flooded flow" (a manifold
operation similar to the report of Brown and Ruzicka\textsuperscript{97} was used) showed poor
reproducibility of signals. Precision was improved only with solvent compensation.

Tyson\textsuperscript{35} studied the effect of air compensation on the absorbance of Pb at carrier
flow rates of 0.72 - 3.4 ml min\textsuperscript{-1}. The nebuliser (fixed nebuliser) liquid uptake was
optimised to about 4 ml min\textsuperscript{-1}. The sensitivities of steady state absorbances, FI-
peak areas and peak heights were all decreased with air compensation compared to
continuous streaming without air compensation. The precision of peak areas
improved with air compensation at carrier flow rates of less than 1.1 ml min\textsuperscript{-1} (8.7% RSD with air and 15% without air at 0.7 ml min\textsuperscript{-1}). This precision, however,
became worse at pumping flow rates greater than 1.5 ml min\textsuperscript{-1} (18% RSD with air compensation and 6.2% without air compensation at 3.4 ml min\textsuperscript{-1}). The precision
of peak heights, on the other hand, was much improved with air compensation,
especially as the carrier flow rates decreased (5% RSD with air and 15% without air
at 0.7 ml min\textsuperscript{-1}). These results, obtained with peristaltic pumping and without pulse
dampers on line, are contrary to those of Garcia\textsuperscript{54} and Sweileh and Cantwell.\textsuperscript{100}

Fang and Welz\textsuperscript{205} conducted an extensive study of Pb and Ca at carrier pumping
flow rates of 0.2 - 6.0 ml min\textsuperscript{-1}. The nebuliser liquid uptake was varied in the range
of 0 - 10.2 ml min\textsuperscript{-1}, with and without air compensation. The workers compared
their results with those obtained by conventional nebulisation. The sensitivity of FI-
peak heights was found to be very much dependent on adjustments of the nebuliser
such that best sensitivities occurred at nebuliser liquid uptake above 6 ml min\textsuperscript{-1} with
FI- pumping flow rate between 3 - 6 ml min\textsuperscript{-1}. This set of conditions corresponds to "starved flow" without air compensation. The adjustments of the nebuliser liquid
uptake rate below 6 ml min\textsuperscript{-1} produced the same trend of observations as made by
Brown and Ruzicka\textsuperscript{97} and their results on air compensation were in agreement with
those reported by Tyson.\textsuperscript{35} The study of the detection limits by these authors\textsuperscript{205}
showed that the peak height quantification of Pb with air compensation produced the
best detection limits especially when the flow spoiler was absent from the nebuliser.
This latter observation, however, seemed contradictory to the lower sensitivities
offered by air compensation without spoiler.

All these conflicting observations in the operation of flame FI-AAS result from the
complexities of atom production in the nebuliser- spray chamber system, the designs
and hence the performances of which vary from one manufacturer to another.\textsuperscript{83,106} Tyson,\textsuperscript{35} in an in-depth discussion of these conflicts, recommends the operation of FI- flame AAS to achieve targeted benefits. The system operation should be at low flow rates to minimise stable compound interference. Otherwise, this operation should be at the conditions that offer maximum SNR so as to achieve best detection limits. Detection limits are to be deduced from the measurements of concentrations for which signals approach those which cannot be distinguished from the random fluctuations of a blank response.

The proposed and on going investigations into the the methods of achieving maximum SNR for transient responses in FI- flame AAS are as follows:

(a), modification of existing nebuliser designs to achieve precise control of the capillary adjustment in its venturi;\textsuperscript{43} (b), modification of the nebuliser system to achieve some specific geometries with\textsuperscript{35} or without\textsuperscript{96} reducing the internal volume of the spray chamber; and (c), a redesign of the nebuliser system to accommodate a heating aerosol chamber for the complete volatilisation of the sample.\textsuperscript{44,92} All these, as well as the existing conventional nebuliser- spray chamber systems, would have to be carefully characterised for the potentials of FI- flame AAS coupling to be fully realised. Therefore the aims of this research are:

(i), optimisation of the nebuliser system of a Baird atomic absorption spectrometer, particularly with respect to the adjustment of the capillary tip in its venturi nozzle and the FI-response characteristics of this system with and without air compensation;

(ii), feasibility of eliminating well documented solute volatilisation interferences such as calcium- phosphate and calcium- aluminium, using instrument optimisation only or with sample solution chemistries in FI- flame AAS. Precipitation- dissolution processes were selected for on-line solution chemistry. Relatively cheap and available reagents such as NH\textsubscript{3}(aq.) and its salts are to replace expensive lanthanum(III) salts and EDTA for matrix conditioning;

(iii), incorporation of cheap membrane filters such as polystyrene and nylon for the on-line solid/liquid separations; and,

(iv), the application of the developed methodologies to trace and real sample analysis.
REFERENCES


CHAPTER TWO

PRELIMINARY STUDIES

2.1. CHARACTERISATION OF NEBULISER SYSTEM

Atom production in flame atomic absorption spectrometry is commonly through the use of nebuliser- spray chamber- burner system, in which a liquid is turned into an aerosol that is finally converted into atoms by the flame. Other techniques of atom production such as electrothermal, laser ablation and vapour generations exist for special applications. Hence, the use of pneumatic nebuliser systems is considered to be the standard method of atom production for most routine atomic spectrochemical analysis.4,5

The pneumatic nebuliser consists of capillary tubing through which a liquid is drawn out as a filament by high pressure gas (about 30 psi pressure) travelling at sonic or supersonic velocity. The filament instantaneously breaks into droplets of varying sizes thus generating a polydisperse primary aerosol.6 The liquid to gas flow ratio determines the size distribution of the aerosol droplets. For a concentric nebuliser, this flow ratio is also affected by the penetration of the capillary tip into the gas venturi nozzle. A nebuliser that generates a primary aerosol with large mean droplet size would cause reduced analyte mass transport to the atomiser. This is because the spray chamber modifies the aerosol drop size distribution by the removal (loss) of larger droplets. The reduced aerosol concentration reduces the sensitivity of analyte signal. In addition, a high fraction of large droplets, on reaching the atomiser, would be desolvated to large particles. The slow vaporisation of the particles, in flame AAS, causes solute volatilisation interference such as the depression of calcium absorbance by phosphate.4,28 Moreover a reduced range of the final droplet size distribution that reaches the atomiser would favour reduced signal noise. The relevant literature reports on the studies carried out to afford an understanding of the analytical performance of the nebuliser system in atomic spectrometry is presented.

The nebuliser liquid flow rate is related to the effective pressure difference between the ends of the capillary (called nebuliser suction), the viscosity of the liquid and the dimensions of the capillary tube by the Hagen- Poiseuille equation (Equation 2.1).

\[ Q = \pi r^4 \Delta P \left( \frac{8 \mu \text{L}}{1} \right) \]  

.................................................. 2.1

44
where \( Q \) is the liquid flow rate, (cm\(^3\) s\(^{-1}\)); \( \pi \) is a constant; \( r \) is the radius of the capillary (cm); \( \Delta P \) is the effective pressure differential (dynes cm\(^{-2}\)), which could be less than the total pressure differential by an amount that is determined by the surface tension effects at the end of the tube; \( \mu \) is the viscosity of the liquid (g cm\(^{-1}\) s\(^{-1}\)); and \( L \) is the length of the capillary (cm).

The equation assumes laminar flow, requiring a Reynolds number of less than 2300. However, Skogerboe and Freeland\(^9\) reported that the equation fails at nebuliser liquid draw rates in excess of 0.6 ml min\(^{-1}\). Reynolds number for these flow rates exceeds 2300 which indicates the predominance of turbulent flow. Skogerboe and Freeland\(^9\) used linear regression mathematical models to interpret the dependence of liquid flow rate on effective pressure difference as well as on nebuliser gas flow rate. The practical effect is that suction is most affected by the position of the nebuliser capillary tip in its nozzle. This in turn affects the liquid flow rate. Sturman\(^10\) and O'Grady et al.,\(^11,12\) have also presented mathematical models which relate nebuliser suction to liquid flow rate with a recommendation that the nebuliser should be operated at maximum suction in order to offset the static head pressure variation of the liquid reservoir.\(^10\)

The droplet size distribution of a primary aerosol is such that the diameter of the droplet, whose volume-to-surface area ratio is the mean of the distribution, is in the order of 10 \( \mu \)m or less.\(^13\) The empirical equation of Nukiyama and Tanasawa,\(^14\) (Equation 2.2) is generally used to relate this distribution to the nebuliser parameters such as the flow rate of the nebulising gas, the flow rate of the liquid, the viscosity, density and surface tension of the liquid.

\[
d_s = \frac{585}{V} \left( \frac{\eta}{\rho} \right)^{0.5} + 597 \left[ \frac{\mu}{(\eta \rho)^{0.5}} \right]^{0.45} \left[ \frac{1000 Q_l}{Q_g} \right]^{1.5} \tag{2.2}
\]

where \( d_s \) is the Sauter mean diameter (\( \mu \)m); \( V \) is the velocity difference between gas and liquid flows (m s\(^{-1}\)); \( \eta \) is the surface tension of the liquid (dyne cm\(^{-1}\)); \( \rho \) is the density of the liquid (g cm\(^{-1}\)); \( \mu \) is the viscosity of the liquid (poise); \( Q_l \) is the volume flow rate of liquid (cm\(^3\) s\(^{-1}\)); and \( Q_g \) is the volume flow rate of gas (cm\(^3\) s\(^{-1}\)). This equation is defined for: 0.8 < \( \rho < 1.2; \) 30 < \( \eta < 73; \) and 0.01 < \( \mu < 0.8.\)
However, present knowledge of the mechanism of the production of a primary aerosol by a pneumatic nebuliser which aspirates at 2 ml min$^{-1}$ is that: beads of liquid are formed at the capillary-jet tip; the beads tend to spread to form films on the surrounding surfaces by capillary action; following which droplets are produced through the stripping-off of the fluids from the beads and films by the nebuliser gas flowing with a sonic or supersonic velocity.\textsuperscript{4,8,15} This mechanism is contrary to the free jet mechanism obtained on a jet-injection nebuliser of large dimensions which was used by Nukiyama and Tanasawa. In addition, the nebuliser gas-flow was operated at below sonic velocity of roughly 340 m s$^{-1}$.\textsuperscript{4} Hence the equation as derived, does not accurately represent the behaviour of analytical nebulisers. The works of Sharp,\textsuperscript{4} Dymott and Widmer\textsuperscript{16} and Gustavsson\textsuperscript{17} show discrepancies between the experimentally measured droplet sizes and those calculated using the empirical equation. In a recent report, Canals and coworkers\textsuperscript{18} showed that the equation consistently overestimated the mean droplet sizes of organic solvents in comparison with water. Moreover, for improved sensitivity and reduced solute volatilisation interferences in flame AAS, atomisation conditions in the flame require a droplet size distribution over a small range of diameters with a median value in the order of 1 $\mu$m (ideally a monodisperse aerosol).\textsuperscript{19-25} Also, there must be an efficient conversion of the liquid to the droplets of the required sizes. Therefore nebuliser designs incorporate impactors such as beads, cups and paddles, as well as appropriate spray chamber geometry such as flow-reversal or cyclonic chambers to produce the finest possible droplets to reach the flame.\textsuperscript{20,26,27} Impactors have been shown to produce smaller droplet sizes by shattering large droplets, by particle/droplet bounce or renebulisation of deposited liquid. This action generates the secondary aerosol.\textsuperscript{28} Further modifications on the secondary aerosol, such as gravitational settling, centrifugal turbulence and/or further impactions cause the larger droplets to settle out finally generating the tertiary aerosol that reaches the flame\textsuperscript{29,30} as shown in Fig. 2.1. Many workers such as Browner and coworkers\textsuperscript{6,15,22} and Routh\textsuperscript{32} reported the droplet size distribution of the emergent tertiary aerosol from the nebuliser- spray chamber combination to be in the range of 0 - 9 $\mu$m or more. The effectiveness of these aerosol modifiers to remove droplets is measured by the droplet cutoff diameter of the spray chamber.\textsuperscript{30}

Attempts to relate the droplet size distribution of the tertiary aerosol to the readily measurable instrument and sample parameters such as nebuliser gas flow rate and liquid uptake rate resulted in mathematical expressions which in general inadequately account for the many complex processes that occur in the nebuliser system. Therefore, the use of semi-empirical models such as the mixing tank model reported
Fig. 2.1. Schematic diagram of a pneumatic concentric nebuliser-spray chamber system.

by Tyson and coworkers\textsuperscript{33-35} provides an insight into the overall nebuliser action. This model successfully explained nebuliser wash-out behaviour as well as transient absorbance profiles in FI-flame AAS.

There are various approaches for measuring droplet size distribution as shown in Table 2.1. A low angle forward scattering of laser light as modified by Mohamed et al.\textsuperscript{36} and collection of droplets on the sequential stages of a cascade impactor are considered to be less tedious and offer reliable results.\textsuperscript{31} The method of direct aerosol collection with membrane filters\textsuperscript{37,38} offers a better precision for the measurement of analyte transport efficiency. However, the claims that analyte transport efficiencies measured by indirect waste collection are less reliable in comparison to those of direct measurements is controversial. Each method has its inherent errors such as evaporation losses and other incomplete recoveries as reported by Ripson and De Galan,\textsuperscript{40} Browner and Smith\textsuperscript{39} and Gustavsson.\textsuperscript{38} In principle, an analyte transport efficiency measured by a differential weighing of the waste from a well equilibrated aerosol, as reported by Maessen et al.,\textsuperscript{41} should offer reliable results. But there are few data reports in both AAS and ICP-AES systems to buttress such merit for the method. This could be due to the method defining
Table 2.1. Some aerosol measuring techniques for the nebuliser systems in Atomic Spectrometry.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Application</th>
<th>Comments</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Laser diffraction with computer ised readout.</td>
<td>drop-size distribution and transport efficiency of ICP nebulisers.</td>
<td>accurate in 2 - 20 µm; drop diameter range; unobtrusive to aerosol processes; fast procedure.</td>
<td>18, 31, 36, 46.</td>
</tr>
<tr>
<td>2. Cascade impactor.</td>
<td>drop-size distribution of AAS and ICP nebulisers.</td>
<td>accurate in 0.1 - 11 µm; solutes analysed; affected by aerosol processes; slow procedure.</td>
<td>20, 22, 23, 48 - 50.</td>
</tr>
<tr>
<td>3. Adsorption tubes:  of silica gel or active charcoal.</td>
<td>transport efficiency of ICP systems.</td>
<td>collects all droplets; solvents analysed.</td>
<td>37, 51.</td>
</tr>
<tr>
<td>4. membrane Filters: (0.3/1.0 µm pore size combination).</td>
<td>transport efficiency of AAS and ICP systems.</td>
<td>collects &gt; 0.2 µm droplets; solutes analysed.</td>
<td>37, 38.</td>
</tr>
<tr>
<td>5. waste collection: (with water or HNO3 washout).</td>
<td>transport efficiency of AAS and ICP systems.</td>
<td>poor RSD (≥ 130%); affected by variable washout times.</td>
<td>37, 38, 52, 53.</td>
</tr>
<tr>
<td>6. Differential weighings.</td>
<td>transport efficiency of ICP systems.</td>
<td>equilibrated aerosol analysed; unobtrusive to nebulisation processes.</td>
<td>41, 54, 55.</td>
</tr>
<tr>
<td>7. MgO/dye coatings with microscope sizing.</td>
<td>drop-size distribution of AAS systems.</td>
<td>applied for &gt; 20 µm; laborious procedure; applied for comparative study.</td>
<td>25, 52.</td>
</tr>
</tbody>
</table>
solution rather than analyte throughput. At present, the common literature value of analyte transport efficiency is about 10% for AAS and 1% for ICP-AES with values varying from one nebuliser system to another.\textsuperscript{30}

It is well recognised that transport efficiency increases as the nebuliser liquid flow rate decreases. This phenomenon, however, does not offer increased signal due to the reduced analyte mass transport. Therefore, a quest for increased transport efficiency at increased analyte transport to the atomiser in microsampling techniques such as FI-AS and HPLC-AS is witnessing a redesign of the nebuliser system. Such nebuliser systems incorporate spray chambers of reduced volumes which are sometimes heated to desolivate the vapour flux or are without impactors.\textsuperscript{42,43,92} The designs have improved transport efficiencies by ten fold or more but possible inefficient heat transport from the chamber walls to the aerosol could aggravate memory effects through salt build-up.\textsuperscript{28} Also, if a high fraction of large droplets reaches the atomiser, then matrix interferences could worsen in AAS.\textsuperscript{15} For these reasons, a heated chamber with jet-vapour-separator\textsuperscript{44,56} (polymer membrane separator for organic solvents\textsuperscript{57}) as reported by Gustavsson should offer better control of the vapour flux.

The performance of a nebuliser system is best evaluated by the measurement of aerosol drop-size distribution curves and analyte transport efficiency. However, the necessary equipment such as cascade impactor and laser diffraction systems may not be available in some laboratories. Hence, other analytical performance criteria such as interference factors from well documented calcium-phosphate system, characteristic concentrations, signal to noise ratios, detection limits, working linear range, noise (error) on signals, matrix salt tolerance and washout time have been applied to assess the merits of the nebuliser system in routine analysis.\textsuperscript{28,29,58} Many of these parameters such as interference factor and characteristic concentration are the direct consequences of droplet size distribution and nebuliser transport efficiency. They are readily deduced from the recorder signals of the standard(s) and/or the calibration curves of results.

Finally, safety of operation and cost (in terms of gas consumption) of nebulisers are additional performance criteria. Nebuliser parts are traditionally machined from metal or constructed from glass to prevent potential metal ion contamination, although constructions with glass are more intricate and difficult. Some nebuliser parts are machined from plastics such as Tygon\textsuperscript{45,46} to reduce corrosion, fragility and costs. Drainage systems are improved to reduce the risks of explosion.\textsuperscript{28} There
has been a report of burners that avoid flash-backs for AES.\textsuperscript{47} The design features of the commercially available nebulisers for atomic spectrometry\textsuperscript{4,15} are presented in Table 2.2.

**Table 2.2.** Commercially available nebulisers for Atomic Spectrometry

<table>
<thead>
<tr>
<th>DESIGN TYPE and Principle</th>
<th>Performance</th>
<th>Comments</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. pneumatic nebulisers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) concentric: liquid flow through an orifice over which a high pressure gas flows.</td>
<td>(standard).</td>
<td>present in nearly all modern AAS used for routine analysis.</td>
<td>5, 25, 52, 59</td>
</tr>
<tr>
<td>(ii) cross flow: spirating needle set so that liquid filament crosses the gas stream from another needle.</td>
<td>reasonable detection limit and sensitivity at low nebuliser gas flow rate.</td>
<td>fragile and difficult machining results in inconsistent manufacture; used for ICP-AES and AES.</td>
<td>60 - 62</td>
</tr>
<tr>
<td>(iii) Babington: nebuliser gas flow through an orifice and liquid flow over the orifice.</td>
<td>detection limit and sensitivity inferior to concentric flow nebuliser.</td>
<td>slurry capability; originally designed for AAS; also suitable for AES and ICP-AES.</td>
<td>45, 46, 63 - 65</td>
</tr>
<tr>
<td>2. ultrasonic: uses electronics to drive the piezo-electric transducer onto which a liquid is continuously pumped.</td>
<td>superior sensitivity and detection limit; droplet formation is independent of gas flow rate.</td>
<td>absence of capillary tube hence clogging is absent; inconvenient sample changing; exhibits memory effects; requires cooling; used for ICP-AES.</td>
<td>8, 66 - 70</td>
</tr>
</tbody>
</table>
Other designs such as thermospray, low pressure jet impact, high pressure nebulisation and monodisperse aerosol generators were reported for fundamental studies in ICP-AES.

In the study reported in this chapter, the performance of a Baird-Atomic atomic absorption spectrometer was evaluated with respect to precision and sensitivity when its nebuliser was operated at conventional aspirations and at controlled-flows offered by flow injection analysis. The figures of merit such as characteristic concentration, working linear range, signal noise and tolerance to matrix condition (salt content and viscosity), as well as analyte transport efficiency were evaluated.

The Baird-Atomic atomic absorption spectrometer has a pneumatic, concentric nebuliser (of fixed adjustment from the manufacturer) that was amenable to adjustments of the capillary tip in its venturi nozzle. Hence the effect of the capillary tip adjustment on the aforementioned figures of merit was also studied.

Elements such as copper and magnesium have been shown to atomise completely in the air-acetylene flame and the absorbance of magnesium is relatively unaffected by a limited variation in the flame conditions. Therefore magnesium analysis, in air acetylene flame, was studied in the optimisation of the spectrometer. This optimisation was a prelude to further studies on air compensation and solute volatilisation interferences in the analysis of calcium, which are presented later in chapter three.

2.2. APPARATUS

The atomic absorption spectrometer (Baird-Atomic, Model A3400) was connected to a Philips AR55 chart recorder for absorbance measurements. The pneumatic concentric nebuliser of the spectrometer has the capillary fixed in its housing by a screw-cap as shown in Fig. 2.2. The screw-cap was turned repeatedly to offer variable adjustments of the nebuliser capillary tip in its venturi nozzle. The nebulising gas was supplied by an air-compressor except for a section on the studies of capillary tip adjustments when an air-cylinder was used to maintain a constant air flow. For the measurement of analyte transport efficiency, the nebuliser outlet tube was adapted to collect drains into a receiver as shown in Fig. 2.3.(iii).

Single line manifolds, shown in Fig. 2.3, were used for FIA. The manifolds were
Fig. 2.2. Experimental scheme for the study of the Baird A3400 nebuliser system.
A, length of tubing attached to the capillary tube; B, displacement of the capillary housing; C, capillary tip adjustment; D, displacement of the impact bead.

(i) 

(iii) 

Fig. 2.3. Apparatus for the preliminary studies of the nebuliser system. (i), single line manifold for controlled-flows; (ii), single line manifold for flow injection analysis; and (iii), nebuliser drainage adapted for indirect analyte-waste collection.
constructed from PTFE tubing (internal diameter, 0.58 mm). The peristaltic pump was a LKB model 2132 Micro Perpex, furnished with PVC pump tubing (internal diameter, 2.79 mm). When a 4-way rotary valve (Rheodyne 5041) was incorporated into the manifold, the pump was replaced with a Gilson Minipuls-2 to offer the carrier flow rates $\geq 10$ ml min$^{-1}$. The arms of the 4-way rotary valve were connected to standard sample loops to offer injection volumes greater than 70 µl. The precoil was a coiled PTFE tube (length, 30 cm, i.d., 0.58 mm and coil diameter, 1 cm). The pulse damper used in later experiments was a T-connector constructed from glass tube (i.d., 0.6 mm) and fitted with a pump tubing (length, 6 cm and i.d., 2.79 mm) closed at one end by welding in a flame.

2.3. REAGENTS

Magnesium solutions were prepared by diluting stock 1000 mg l$^{-1}$ solutions (BDH SpectrosoL grade). Glycerol (50%, m/v) used to create viscous effect and sodium chloride solution (25%, m/m) used as the concomitant, were prepared from the BDH AnalAR compounds. Reagent-grade water (LiquiPure RG system; reverse osmosis followed by ion-exchange) was used for making up the solutions and for the carrier streams.

2.4. PROCEDURES AND RESULTS

2.4.1. Optimisation of Baird-Atomic (A3400) spectrometer

The manufacturer's absorption performance data for magnesium$^{81}$ were used to start off the adjustments of the spectrometer. The power supply to the spectrometer was switched on to permit the instrument to warm up without operating the nebuliser-burner system for a period of about 15 minutes. The slit width was set at 2. Then the EHT (extra high tension power supply) coarse control, wavelength scan and lamp current were adjusted in unison to give maximum absorbance of 0.8 at the wavelength, 285 nm, and at a current of 3 mA.

The nebuliser was operated with the manufacturer's adjustments, that is, the capillary screw-cap was tightened such that the capillary tip was about 2 mm out of its barrel. The impact bead was set as close to the capillary tip as the instrument design permitted. The flame was ignited with air flow rate set to remain at 7.5
Fig. 2.4. Effect of instrument parameters on the absorbance of 0.5 mg l\(^{-1}\) Mg. (i), acetylene flow at air flow rate, 7.5 l min\(^{-1}\); (ii), burner position at air + acetylene flows, [7.5 + 3] l min\(^{-1}\); (iii), lamp current at air + acetylene flows, [7.5 + 3] l min\(^{-1}\) and burner height, 4 cm.
1 min⁻¹ and acetylene flow rate at 2 l min⁻¹. The scale expansion and curve correction were set to 1.0 and linear. Reagent grade water was aspirated to zero absorbance and 0.5 mg l⁻¹ Mg were sprayed to maximise absorbance readings as the instrument was adjusted with respect to flame conditions (the variation in the acetylene flow rate, burner height, and burner traverse position) and lamp current. The results of these adjustments are shown in Fig. 2.4. The final settings for the optimised spectrometer are shown in Table 2.3.

The normal calibration procedure for the determination of magnesium, when the spectrometer was set at these optimum conditions, was carried out. Water was aspirated to zero the absorbance followed by the series of standard solutions shown in Table 2.4. The absorbances obtained were plotted against concentration as shown in Fig. 2.5.

In the normal calibration graph of magnesium, the linear range of 0 - 0.5 mg l⁻¹ offers minimum residual errors⁸² with a sensitivity (characteristic concentration) of 0.004 mg l⁻¹. This experimental characteristic concentration, 0.004 mg l⁻¹, compared favourably with the manufacturer’s value of 0.005 mg l⁻¹. Therefore the spectrometer was deemed to function properly.

Table 2.3. Optimum conditions for the determination of magnesium on Baird (A3400) spectrometer

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength, nm</td>
<td>285.2</td>
</tr>
<tr>
<td>Slit width, nm</td>
<td>0.5</td>
</tr>
<tr>
<td>Lamp current, mA</td>
<td>2</td>
</tr>
<tr>
<td>Supporting gas/flow rate, l min⁻¹</td>
<td>air/7.5</td>
</tr>
<tr>
<td>Fuel gas/flow rate, l min⁻¹</td>
<td>acetylene/3.0</td>
</tr>
<tr>
<td>Burner height, cm</td>
<td>4</td>
</tr>
<tr>
<td>Read out</td>
<td>direct</td>
</tr>
<tr>
<td>Scale expansion</td>
<td>1</td>
</tr>
<tr>
<td>Curve correction</td>
<td>linear</td>
</tr>
<tr>
<td>Damping</td>
<td>off</td>
</tr>
<tr>
<td>Impact bead reference point</td>
<td>reference point*</td>
</tr>
<tr>
<td>Capillary tip adjustment</td>
<td>reference point*</td>
</tr>
</tbody>
</table>

* manufacturer’s reference
Table 2.4. Absorbance readings of standard solutions of magnesium at conventional aspirations of Baird, Model A3400, spectrometer

<table>
<thead>
<tr>
<th>solution</th>
<th>concentration, mg l(^{-1})</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00</td>
<td>0.000 ± 0.002</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.113 ± 0.002</td>
</tr>
<tr>
<td>3</td>
<td>0.25</td>
<td>0.270 ± 0.002</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
<td>0.435 ± 0.005</td>
</tr>
<tr>
<td>5</td>
<td>0.50</td>
<td>0.560 ± 0.005</td>
</tr>
<tr>
<td>6</td>
<td>0.60</td>
<td>0.650 ± 0.005</td>
</tr>
<tr>
<td>7</td>
<td>0.75</td>
<td>0.790 ± 0.010</td>
</tr>
<tr>
<td>8</td>
<td>1.00</td>
<td>* reading out of scale</td>
</tr>
</tbody>
</table>

* reading out of scale

Regression equation for linear portion of graph:

\[ A = -0.001 + 1.11 \times C \]

\[ R = 0.999 \]

Fig. 2.5. Normal working curve for magnesium at 285.2 nm

[A, absorbance; C, concentration, and R, Pearson's correlation coefficient.]
2.4.2. Effect of the adjustments of the impact bead

The spectrometer was set to operate as in Table 2.3. The support arm of the impact bead was pulled fully out of the spray chamber to place the impact bead at the manufacturer's reference (that is, as close to the capillary tip as the nebuliser design permitted). The arm was marked from this position at 2 mm intervals outwards. Water was aspirated followed by the 0.5 mg l⁻¹ Mg at each position of the impact bead as the support arm was pushed into the spray chamber. The optimum absorbance decreased as the impact bead was moved away from the capillary tip as shown in Fig. 2.6.(i). This figure shows that absorbance rapidly decreased to 50% of its optimum value within a 6 mm displacement. The noise level also increased within this interval. The absorbance finally levelled to 40% of its optimum value at the displacements of 10 mm and more.

The normal calibration of the spectrometer for magnesium analysis was carried out at three different impact bead positions. The resulting analytical curves are shown in Fig. 2.6.(ii). The curves were linear but the sensitivity decreased as the distance between the impact bead and the capillary tip increased.

2.4.3. Effect of the length of polythene tube attached to the nebuliser capillary tube

The spectrometer was operated at optimum conditions as in Table 2.3. Different lengths of polythene tube were attached to the nebuliser capillary and for each attachment, water was aspirated to zero the absorbance followed with the aspiration of 0.5 mg l⁻¹ Mg. The sample cup was placed in the sample holder so that the aspirating and suction ends of the nebuliser system were at the same level for all measurements. For each tube, the mass of water taken up by the nebuliser in two minutes, the average of two consecutive results and the weight of water per minute calculated from the average was the liquid uptake rate in ml min⁻¹ (the density of water was assumed to be 1 g cm⁻³). As the length of the polythene tube increased, the suction rate as well as the corresponding absorbance decreased as shown in Fig. 2.7 A. The considerable scatter in the plot of uptake rate against tube length could be due to a parameter such as pressure drop between the aspirating and suction ends of the capillary, which the design of the experiment failed to control precisely. Nevertheless the graph of absorbance against uptake rate, as shown in Fig. 2.7.A(ii) shows statistical reliability. The curve progressed to a maximum which offered an optimum liquid uptake rate of 5.5 ml min⁻¹ with 0.520 absorbance.
Fig. 2.6. Adjustment of the impact bead.
(i), effect on the absorbance of 0.5 mg l⁻¹ Mg;
(ii), effect on normal calibration curve of Mg: bead displacements, 0 mm, (○); 2 mm, (●); and 10 mm, (▲).

(A, absorbance; C, concentration; and R, Pearson's correlation coefficient.)
The experiment was carried out for the aspirating end above the suction end of the capillary tube as suction from a long-necked flask. The results, Fig. 2.7.B, are similar to the results for both ends kept at the same level. Thus the size and shape of the sample container had no significant effect on the optimum absorbance as long as the short length of tubing that offered the optimum liquid uptake rate was used.
All the polythene tubes, except the tube indicated, were of the same inner diameter that fitted the nebuliser capillary tube tightly. The tube having the arrowed data had a slightly larger inner diameter than those tested and so did not fit the nebuliser capillary end tightly. The subsequent effect was the ingress of air at the loose connections which gave lower and inconsistent suction rates than the trend of results (see Fig. 2.7).

2.4.4. Adjustment of the nebuliser capillary tip in its venturi nozzle

In accordance with experiment 2.4.3, the tube (length 7.2 cm) that offered the optimum liquid uptake rate of 5.5 ml min\(^{-1}\) and the optimum absorbance of 0.520 for 0.5 mg l\(^{-1}\) Mg, was attached to the nebuliser capillary tube. The nebuliser capillary tip at its reference position was jutting out of its housing/septum by 2.0 mm. An anti-clockwise rotation of the capillary screw cap caused the capillary tip to recede into its septum such that 2.26 revolutions of the cap was equivalent to a translational movement of 2.0 mm. Therefore 1 revolution (circumference of cap) caused a displacement distance of 0.88 mm. For this experiment, the circumference of the capillary screw cap was marked into four equal parts to permit analytical measurements at 0.22 mm intervals or multiples thereof. The spectrometer was operated at the optimum conditions as in Table 2.3. For each position of the capillary tip, water was aspirated to zero the absorbance followed by 0.5 mg l\(^{-1}\) Mg for the absorbance reading. The liquid uptake rate at each position of the capillary tip was determined gravimetrically as in experiment 2.4.3.

The plots in Fig. 2.8 show that the liquid uptake rate increased to a maximum of 10 ml min\(^{-1}\) as the capillary tip receded a distance of 3.5 mm (away from the impact bead). The liquid uptake rate decreased with further displacement till gas bubbles appeared in the test solution. Initially the absorbance of the test solution increased uniformly as the uptake rate increased and peaked at 6.7 ml min\(^{-1}\). Then the absorbance decreased for further high values of the liquid uptake rate. The absorbance maximum occurred at a capillary tip displacement of 2.5 mm, a situation in which the capillary tip receded and just entered into its septum/housing.

During the experiment, the air flow increased from 7.5 l min\(^{-1}\) to 9 l min\(^{-1}\). Therefore the effect of the adjustment of the capillary tip, whilst keeping both the fuel and the oxidant flow rates constant, was studied. Compressed air from a cylinder was used, instead of the compressor-pump, to supply air to the nebuliser. The air offered smooth and non-pulsating flows such that air flow rate was
Fig. 2.8. Adjustment of the nebuliser capillary tip.
(i), effect on liquid uptake rate and hence on the absorbance of 0.5 mg l$^{-1}$ magnesium; (ii), plot of absorbance against liquid uptake rate of 0.5 mg l$^{-1}$ magnesium. During the experiment, air flow rate varied without adjustment.
Fig. 2.9. Capillary tip adjustment at constant air flow rate of 7.5 ml min⁻¹:
(i), effect on the nebuliser liquid uptake rate and absorbance of 0.5 mg l⁻¹ Mg;
(ii), plot of absorbance against the uptake rate of 0.5 mg l⁻¹ Mg.
rate increased to a maximum (albeit a plateau of lower value, 8 ml min\(^{-1}\)) at a similar capillary tip displacement of 3.5 mm, as in the earlier experiment. Then, the uptake decreased to a fairly constant value of 6.8 ml min\(^{-1}\). The absorbance of 0.5 mg l\(^{-1}\) Mg, however, exhibited oscillations the amplitude of which decreased to a fairly constant value as the distance of the capillary tip displacement increased. The plot of absorbance against uptake rate also exhibits oscillations but of no particular trend. The colour of the flame turned from bluish to yellowish as the experiment progressed (that is, as the distance of the capillary tip from the impact bead increased). The adjustment caused increased liquid uptake without increased oxidant flow which in turn reduced the flame temperature, hence the luminous flame. This phenomenon was absent in the earlier experiment. Therefore the optimisation of the nebuliser with respect to capillary tip adjustment, in later studies, was restricted to the region where the air flow rate was undisturbed, at a capillary tip displacement of not more than 3.5 mm.

The normal calibration data for magnesium at different capillary tip displacements showed identical linear range as depicted in Fig. 2.10. The sensitivity was

\[
\begin{align*}
A &= 0.001 + 1.29 C \\
R &= 0.999 \\
A &= 0.010 + 1.03 C \\
R &= 0.999 \\
A &= 0.003 + 0.979 C \\
R &= 0.999
\end{align*}
\]

**Fig. 2.10.** Normal working curves for Magnesium at capillary tip displacements: 0 mm, reference position (○); 2.42 mm, position of maximum absorbance (●); and 3.52 mm, position of maximum uptake rate (□). (A, absorbance; C, concentration; and R, Pearson's correlation coefficient.)
maximum at a position of the capillary tip which did not offer a maximum liquid uptake. Thus the adjustment offered a better sensitivity than the manufacturer's reference position. This occurred when the nebuliser capillary tip just entered into its housing. The sensitivity at maximum liquid uptake rate was lower than the value obtained at manufacturer's capillary tip reference position.

2.4.5. Effect of pushing the nebuliser capillary housing towards the impact bead

The length of the capillary housing was marked at 2 mm intervals. The spectrometer was operated at optimum conditions as in Table 2.4 and the nebuliser capillary tip was adjusted to offer the maximum absorbance for 0.5 mg l⁻¹ Mg. The capillary housing was pushed, at 2 mm incremental displacements, towards the impact bead. At each position of the housing, water was aspirated to zero the absorbance followed by 0.5 mg l⁻¹ Mg. As shown in Fig. 2.11, the absorbance of 0.5 mg l⁻¹ Mg decreased linearly as the distance between the capillary tip and the impact bead decreased. When the capillary housing was pushed to its limit, the absorbance of 0.5 mg l⁻¹ Mg fell sharply with increased noise level and the liquid uptake was sluggish.

Fig. 2.11. Effect of moving the capillary housing towards the impact bead on the absorbance of 0.5 mg l⁻¹ magnesium. (arrowed data is the limit of moving housing towards the impact bead.)
The linear relationship and the stable noise level exhibited by the adjustments, should permit analytical determinations at reduced sensitivities without sacrificing precision thereby increasing the linear range for magnesium. This would be advantageous over the adjustments of the impact bead, capillary tip and length of the polythene tubing attached to the nebuliser capillary for they exhibit more complex absorbance trends.

2.4.6. Operation of the spectrometer with controlled flow of liquid to the nebuliser

The manifold shown in Fig. 2.3.(i) was used. The spectrometer was operated at the optimum conditions shown earlier in Table 2.4. The peristaltic pump used to deliver the continuous stream of liquid to the nebuliser was calibrated gravimetrically by the method of weighing by difference. The mass of water delivered for fixed times, at different pumping flow rates, was noted. The pumping flow rate was varied by adjusting the setting of the pump's potentiometer. The pumping rate was calculated as the volume of water pumped in a unit time in millimetres per minute. For the calculation, the density of water was approximately 1 g cm$^{-3}$ at 25 °C, the laboratory temperature.

Fig. 2.12. Calibration graph for Gilson Minipuls-2 peristaltic pump. (y, pumping rate; x, pump meter setting; and R, Pearson's correlation coefficient.)
Fig. 2.12 shows a linear trend of results for the Gilson Minipuls-2. The intercept on the y-axis of graph would be the additional effect of the nebuliser suction which manifested itself through the manifold. Therefore pumping rates had to be determined at every data stage of this report so as to correct for the possible errors which could arise from an inconsistent nebuliser-burner effect during a lengthy operation of the spectrometer.

2.4.6.(I). Effect of pumping rate on the absorbance of magnesium/nebuliser transport efficiency

The spectrometer was operated at optimum conditions with the capillary tip just withdrawn into its housing. The nebuliser drain outlet was adapted to drain into a 250 ml polythene bottle as in Fig. 2.3.(iii). The transparent plastic tube, as coiled, emptied its drain completely (by spurting) at short intervals of about 25 seconds. Using the manifold in Fig. 2.3 (i), water was pumped to the nebuliser to generate the baseline on a chart (chart speed 10 s cm⁻¹) at zero absorbance with the pump roller speed meter set at 99. Then a weighed solution of 0.5 mg l⁻¹ Mg was pumped through the manifold for a fixed period during which the steady state absorbance of magnesium was recorded and the nebuliser drained into a clean weighed polythene bottle. Water was pumped again and the drainage collection continued for a further five or more successive spurting of the drain. The polythene bottle was replaced with another, weighed, stoppered and stored away for the absorbance of the drain to be later measured by conventional aspiration. This procedure, which was adapted from the method of Wolf and Stewart, was carried out in triplicate at each pump setting. The pumping rates were deduced from the weighings as previously described. The absorbances of 0.5 mg l⁻¹ Mg and of the waste were measured by conventional aspiration and used to calculate the analyte transport efficiency thus,

\[
\text{analyte transport efficiency} = \frac{100 \text{(mass x absorbance)}_{\text{waste}}}{\text{standard}}
\]

The analyte transport efficiency for the Baird A3400 nebuliser was approximately 10% for the liquid flows of 5 - 7 ml min⁻¹ as shown Fig. 2.13. These liquid flow rates also gave optimum absorbance for the spectrometer when either impact bead or nebuliser capillary tip was adjusted. Transport efficiency was not affected by high flow rates of up to 8.5 ml min⁻¹. But efficiency gradually increased to about
Fig. 2.13. Effect of pumping rate on the steady state absorbance of 0.5 mg l$^{-1}$ magnesium and on the nebuliser analyte transport efficiency.
30% as the flow rate decreased below 5 ml min\(^{-1}\). On the other hand, steady state absorbance decreased as the pumping flow rate decreased. Also, the noise worsened as shown in Fig. 2.13. The noise was observed as ripples on the recorded absorbance at a chart speed of 10 s cm\(^{-1}\). A tentative comparison of the steady state absorbances from controlled flows with those of conventional aspiration is presented in Fig. 2.14. The two modes offered similar absorbance at flow rates of 5 - 6 ml min\(^{-1}\) but at high flows, above 7 ml min\(^{-1}\), the controlled flow offered higher and constant absorbance.

![Graph showing absorbance vs. liquid flow rate](image)

**Fig. 2.14.** Comparison of the effect of liquid flow rate on the steady state absorbance of 0.5 mg l\(^{-1}\) magnesium: (i), controlled flow (●); and (ii), conventional aspiration using varied length of tubings (○), and varied positions of capillary tip (+).

Table 2.5 and Fig. 2.15 show that the high and constant absorbance could be reached at any position of the capillary tip. However, the optimum position of the capillary tip offered high and constant absorbance from a lower flow rate of 5 ml min\(^{-1}\). This region of high flow rate has the demerit of low transport efficiency and the peristaltic pumping offered lower signal to noise ratios below 7 ml min\(^{-1}\) (see Table 2.5). Therefore further work in this report incorporated pulse dampers...
and appropriate size of pump tubes (smaller internal diameter for reduced flow rates) into the manifold, to improve the signal to noise ratio and so highlight the merits of controlled flows for FI-flame AAS in the low flow rate region.

Table 2.5. Effect of pumping rate on the steady state absorbance and signal noise of 0.5 mg l⁻¹ magnesium at different capillary tip displacements

<table>
<thead>
<tr>
<th>displacement, 0 mm</th>
<th>displacement, 2.42 mm</th>
<th>displacement, 3.52 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>flow rate</td>
<td>Absorbance</td>
<td>flow rate</td>
</tr>
<tr>
<td>8.76</td>
<td>0.610 ± 0.025</td>
<td>8.74</td>
</tr>
<tr>
<td>8.42</td>
<td>0.605 ± 0.030</td>
<td>8.37</td>
</tr>
<tr>
<td>7.84</td>
<td>0.605 ± 0.030</td>
<td>7.96</td>
</tr>
<tr>
<td>7.39</td>
<td>0.610 ± 0.025</td>
<td>7.62</td>
</tr>
<tr>
<td>6.96</td>
<td>0.605 ± 0.020</td>
<td>7.04</td>
</tr>
<tr>
<td>6.58</td>
<td>0.590 ± 0.025</td>
<td>6.56</td>
</tr>
<tr>
<td>6.18</td>
<td>0.590 ± 0.020</td>
<td>6.15</td>
</tr>
<tr>
<td>5.75</td>
<td>0.590 ± 0.020</td>
<td>5.77</td>
</tr>
<tr>
<td>5.17</td>
<td>0.580 ± 0.020</td>
<td>5.33</td>
</tr>
<tr>
<td>4.89</td>
<td>0.570 ± 0.020</td>
<td>4.90</td>
</tr>
<tr>
<td>4.43</td>
<td>0.555 ± 0.015</td>
<td>4.53</td>
</tr>
<tr>
<td>4.02</td>
<td>0.535 ± 0.020</td>
<td>4.01</td>
</tr>
<tr>
<td>3.58</td>
<td>0.515 ± 0.020</td>
<td>3.58</td>
</tr>
<tr>
<td>3.15</td>
<td>0.490 ± 0.020</td>
<td>3.15</td>
</tr>
<tr>
<td>2.70</td>
<td>0.460 ± 0.020</td>
<td>2.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.80</td>
</tr>
</tbody>
</table>

** 0.495 ± 0.010 ** 0.580 ± 0.010 ** 0.615 ± 0.020

* flow rate measured in ml min⁻¹.
** Absorbance by conventional aspiration.
2.4.6.(II). Effect of pumping flow rate, sample volume and tube length on FI-absorbance peak

The spectrometer was operated at optimum conditions with the capillary tip just withdrawn into its housing and connected to the manifold as shown in Fig. 2.3.(ii). Using a low flow rate of 0.79 ml min\(^{-1}\), the time taken to fill the sample loop when the leading edge of a slug of coloured water moved in and out of the rotary valve was determined. The volume of the loop was calculated as the product of pumping flow rate and time. Hence the volume of the loop which was formed by connecting two arms of the valve was 130 ± 10 µl, the mean of ten determinations.

A study of the effect of pumping flow rate was carried out and water was used as the carrier stream. The sample loop, volume 130 ± 10 µl, was filled with 0.5 mg l\(^{-1}\) Mg, injected into water stream and propelled through a straight tube of 20 cm length, to the spectrometer. The peak height was recorded on chart at 120 s cm\(^{-1}\) (the slow chart movement was used to collapse the noise on the absorbance profiles at low
pumping rates so as to record sharp peaks). Five sample injections were carried out for each pump setting. Also, steady state absorbances were recorded and pumping flow rates were determined as earlier described in section 2.4.6.(1). The results are shown in Table 2.6.(A).

A study of the effect of sample volume was carried out at the pump setting that offered a flow rate of $6.1 \pm 0.1$ ml min$^{-1}$ through the injections of the volumes shown in Table 2.6.(B). The chosen flow rate was in the range of values that offered highest peak height absorbances as shown in Table 2.6.(A). The arms of

Table 2.6. Variation of the absorbance, peak height precision and dilution factor of 0.5 mg l$^{-1}$ magnesium with the manifold parameters in FI-flame AAS

<table>
<thead>
<tr>
<th>pump rate, ml min$^{-1}$</th>
<th>peak height (Hp)</th>
<th>Absorbance (Hs) (steady state)</th>
<th>dilution factor, (Hs/Hp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>$0.068 \pm 0$</td>
<td>$0.080 \pm 0.025$</td>
<td>1.54</td>
</tr>
<tr>
<td>0.47</td>
<td>$0.074 \pm 0.001$</td>
<td>$0.095 \pm 0.020$</td>
<td>1.55</td>
</tr>
<tr>
<td>0.64</td>
<td>$0.095 \pm 0.004$</td>
<td>$0.115 \pm 0.030$</td>
<td>1.53</td>
</tr>
<tr>
<td>0.91</td>
<td>$0.126 \pm 0.006$</td>
<td>$0.155 \pm 0.035$</td>
<td>1.51</td>
</tr>
<tr>
<td>1.47</td>
<td>$0.179 \pm 0.003$</td>
<td>$0.225 \pm 0.035$</td>
<td>1.45</td>
</tr>
<tr>
<td>2.05</td>
<td>$0.218 \pm 0.004$</td>
<td>$0.285 \pm 0.035$</td>
<td>1.47</td>
</tr>
<tr>
<td>2.61</td>
<td>$0.263 \pm 0.003$</td>
<td>$0.345 \pm 0.025$</td>
<td>1.41</td>
</tr>
<tr>
<td>3.27</td>
<td>$0.307 \pm 0.005$</td>
<td>$0.395 \pm 0.020$</td>
<td>1.35</td>
</tr>
<tr>
<td>3.93</td>
<td>$0.328 \pm 0.005$</td>
<td>$0.440 \pm 0.015$</td>
<td>1.34</td>
</tr>
<tr>
<td>4.60</td>
<td>$0.345 \pm 0.005$</td>
<td>$0.475 \pm 0.010$</td>
<td>1.38</td>
</tr>
<tr>
<td>5.33</td>
<td>$0.350 \pm 0.001$</td>
<td>$0.500 \pm 0.015$</td>
<td>1.43</td>
</tr>
<tr>
<td>5.94</td>
<td>$0.342 \pm 0.006$</td>
<td>$0.500 \pm 0.010$</td>
<td>1.46</td>
</tr>
<tr>
<td>6.72</td>
<td>$0.346 \pm 0.005$</td>
<td>$0.510 \pm 0.010$</td>
<td>1.47</td>
</tr>
<tr>
<td>7.30</td>
<td>$0.343 \pm 0.005$</td>
<td>$0.525 \pm 0.010$</td>
<td>1.53</td>
</tr>
<tr>
<td>8.02</td>
<td>$0.333 \pm 0.005$</td>
<td>$0.525 \pm 0.010$</td>
<td>1.58</td>
</tr>
<tr>
<td>8.64</td>
<td>$0.317 \pm 0.004$</td>
<td>$0.525 \pm 0.010$</td>
<td>1.66</td>
</tr>
<tr>
<td>9.29</td>
<td>$0.312 \pm 0.003$</td>
<td>$0.525 \pm 0.010$</td>
<td>1.68</td>
</tr>
<tr>
<td>10.01</td>
<td>$0.304 \pm 0.006$</td>
<td>$0.530 \pm 0.015$</td>
<td>1.74</td>
</tr>
</tbody>
</table>
Table 2.6 continued

(B), effect of injected sample volume; through 20 cm tube length at the pumping flow rate of 6.1 ml min⁻¹

<table>
<thead>
<tr>
<th>sample volume, µl</th>
<th>peak height</th>
<th>dilution factor †</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.216 ± 0.004</td>
<td>2.44</td>
</tr>
<tr>
<td>170</td>
<td>0.334 ± 0.007</td>
<td>1.57</td>
</tr>
<tr>
<td>270</td>
<td>0.386 ± 0.011</td>
<td>1.36</td>
</tr>
<tr>
<td>370</td>
<td>0.413 ± 0.012</td>
<td>1.27</td>
</tr>
<tr>
<td>470</td>
<td>0.436 ± 0.002</td>
<td>1.20</td>
</tr>
<tr>
<td>570</td>
<td>0.486 ± 0.008</td>
<td>1.08</td>
</tr>
<tr>
<td>670</td>
<td>0.476 ± 0.009</td>
<td>1.10</td>
</tr>
<tr>
<td>770</td>
<td>0.512 ± 0.005</td>
<td>1.03</td>
</tr>
<tr>
<td>870</td>
<td>0.522 ± 0.001</td>
<td>1.01</td>
</tr>
<tr>
<td>970</td>
<td>0.520 ± 0.001</td>
<td>1.01</td>
</tr>
<tr>
<td>1070</td>
<td>0.522 ± 0.006</td>
<td>1.01</td>
</tr>
<tr>
<td>2570</td>
<td>0.510 ± 0.015 *</td>
<td>1.00</td>
</tr>
</tbody>
</table>

(C), effect of tube length travelled by the sample slug; for the injection of 70 µl at pumping flow rate of 6.1 ml min⁻¹

<table>
<thead>
<tr>
<th>tube length, cm</th>
<th>Absorbance, (Hₚ)</th>
<th>dilution factor †</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>0.228 ± 0.007</td>
<td>2.30</td>
</tr>
<tr>
<td>55.5</td>
<td>0.187 ± 0.006</td>
<td>2.81</td>
</tr>
<tr>
<td>105.5</td>
<td>0.159 ± 0.002</td>
<td>3.30</td>
</tr>
<tr>
<td>141.0</td>
<td>0.146 ± 0.003</td>
<td>3.60</td>
</tr>
<tr>
<td>193.0</td>
<td>0.124 ± 0.003</td>
<td>4.23</td>
</tr>
<tr>
<td>228.5</td>
<td>0.113 ± 0.002</td>
<td>4.65</td>
</tr>
<tr>
<td>283.5</td>
<td>0.114 ± 0.003</td>
<td>4.61</td>
</tr>
<tr>
<td>314.3</td>
<td>0.112 ± 0.001</td>
<td>4.69</td>
</tr>
<tr>
<td>349.8</td>
<td>0.102 ± 0.003</td>
<td>5.15</td>
</tr>
</tbody>
</table>

* steady state absorbance with noise on signal.
† upper level of the steady state absorbance used to calculate dilution factor.
the valve that formed the sample loop were cut and the volume of the resulting loop determined as 70 ± 6 μl. Standard sample loops were attached to the arms to provide the volumes shown in Table 2.6(B). Five replicate injections were carried out for each sample volume and the flow rate was checked twice in the course of the experiment.

A study of the effect of tube length was carried out. The length of tube from the injection valve to the nebuliser was varied and 70 μl of the magnesium solution were injected into the water stream moving at 6.1 ml min⁻¹. Five replicate injections were carried out for each length of tube and the mean peak heights are shown in Table 2.6(C). The steady state absorbance of Table 2.6(B) was used to calculate the dilution factors.

These results as plotted in Fig. 2.16 show that the Fl- absorbance peak heights are generally lower than the corresponding steady state absorbance at a fixed pumping rate. The Fl- peak height increased as the sample volume increased and with the injection of large volumes, generated the steady state absorbance. The Fl- peak height decreased as the tube length travelled by the sample plug increased and the associated manifold dilution factor increased linearly to an approximate plateau. The precision of the Fl- absorbance ranged from 1 - 5% RSD and, in a similar trend to the noise on the steady state absorbance, became poor as the pumping flow decreased. The absolute precision was better than the steady state noise which in the experiment ranged from 2 to 23 percent of the steady state absorbance. Figure 2.16(i) shows that the manifold dilution factor decreased linearly as the pumping flow rate decreased. The break in the linear trend from 3 ml min⁻¹ and below, corresponded to the significant effect of the pump pulsations which caused the additional increase in the dilution factors. Although the absolute precision of the Fl-peaks seemed unaffected by the pulsations, the signal to noise ratio for the steady state absorbance worsened. Therefore an additional device, such as an on-line T-piece having an air column, would be used as pulse dampers in the manifold. That is, the coiled PTFE tube (length, 30 cm, i.d., 0.58 mm and coil diameter, 1 cm) present in the manifold (in Fig. 2.3(ii)) could not reduce the noise on the steady state absorbance at low pumping flow rates.
Fig. 2.16. Effect of manifold parameters on the absorbance of 0.5 mg l⁻¹ magnesium: (i), pumping rate; (ii), sample volume; and (iii), length of tube traversed by the sample slug. (steady state absorbance $A$, FI-peak height (•), and manifold dilution factor (□).)
2.4.6.(III). Effect of dissolved solids on the absorbance of magnesium.

The spectrometer was operated at optimum conditions and connected to the manifold as shown in Fig. 2.3.(ii).

Ten solutions each containing 0.5 mg l⁻¹ Mg and varied amounts of sodium chloride were used in the experiment. The blanks contained the varied amounts of sodium chloride in water. The solutions and blanks were injected into the water stream at a pumping flow rate of 6.5 ml min⁻¹. Five replicate injections were carried out for each solution and similarly for its blank. The procedure was carried out at the manifold parameters that offered approximate dilution factors of 5, 2 and 1, the steady state absorbance. The absorbance peaks were recorded on a chart at a speed of 60 s cm⁻¹. The mean peak heights of the absorbances were used to plot graphs.

A comparative study was carried out in which the absorbances of the solutions and the blanks were determined at conventional aspiration of the nebuliser. The samples were aspirated in the order, blank, water, solution, water so that blockage of the nebuliser capillary or burner was minimised. The graphs of the results are shown in Fig. 2.17. The blank corrected absorbance, termed net absorbance in the figure, was lower than the absorbance of simple 0.5 mg l⁻¹ Mg for both FIA and conventional aspiration. The higher the amount of the dissolved NaCl, the lower the net absorbance. The absorbance lowering was however gradual at the dilution factor of 5 and the samples neither blocked the nebuliser capillary nor the burner for FIA. The net absorbance was able to show the tolerance of FIA to dissolved solids as due to the dilution effect of the manifold as well as the water stream that continuously washed the nebuliser. The general purpose reagent NaCl, used in the experiments, caused the considerable blank absorbance which could be a result of light scattering as well as an absorbance error from the magnesium present as impurity in the NaCl.
2.4.6. (IV). Effect of sample viscosity on the absorbance of magnesium.

The experimental conditions of section 2.4.6.(III) were applied and the procedures for both FIA and conventional aspiration were repeated. The 0.5 mg l⁻¹ Mg and blanks contained glycerol (% m/v) instead of NaCl. There was no burner or capillary blockage during the experiment. The flame, however, showed some sparks due to burning soots but the condition affected neither the FI- precision nor the steady state absorbance noise significantly. The results were plotted as shown in Fig. 2.18. In the experiment, the blank absorbances were zero or within the noise level of the solution absorbances, hence the blank plots were omitted from the graphs.
The absorbance of 0.5 mg l⁻¹ Mg at conventional aspiration decreased as the concentration of the glycerol increased. The decrement was roughly 1.6% of the absorbance of simple 0.5 mg l⁻¹ Mg for every 1% (m/v) glycerol matrix. The FI-procedure showed a similar trend at steady state but the decrement became gradual as the manifold dilution factor increased. Hence, the decrement at a dilution factor of 5 was roughly 0.26% of the absorbance for 1% glycerol matrix.

The FI-procedure showed a considerable tolerance to the viscosity effect in that a significant decrease in absorbance was delayed until the glycerol matrix was more than 20% at the dilution factor of 2. The effect of dissolved solids showed no such tolerance at the dilution factor of 2 (see Fig. 2.17(ii)). Therefore FI-procedure minimised the effect of viscosity more readily than the effect of dissolved solids on the Baird spectrometer.
2.5. DISCUSSION

Conventional aspiration of the nebuliser_ The pneumatic nebuliser- burner system, at conventional aspiration, acts as a pump and as a subsampler. Therefore the adjustments of the capillary tip in its venturi nozzle and the impact bead in the spray chamber critically control both the pumping and the sampling characteristics of the pneumatic concentric nebuliser. In this work, the impact bead of the Baird nebuliser system offered maximum absorbance at a position which was as close to the nebuliser venturi as the design permitted. Consequently, the absorbance decreased sharply and levelled off at 50% of the maximum absorbance as the impact bead was moved 8 mm away from the venturi (see Fig. 2.6). The existence of a critical position for the impact bead is supported by the works of Dymott and Widmer and Routh. Routh reported an optimum position of the impact bead at 1 - 1.3 mm from the nebuliser, for the Varian Techtron. Similarly Dymott and Widmer observed an optimum position of the impact bead for the Pye Unicam/Philips Scientific instrument. However, the report of O'Grady and coworkers slightly differed. These workers observed a plateau of 2-fold increase in sensitivity for magnesium with the Baird spectrometer. Figure 2 in the reference shows the optimum plateau at the impact bead displacements of 3 mm and more from the nebuliser. The capillary tip was set at maximum liquid uptake/suction in the report of O'Grady and coworkers. This could cause the results to differ from the present work because the capillary tip, at the manufacturer's setting in experiment 2.4.2, was not at optimum suction.

Browner and coworkers and Routh measured the aerosol droplet size distribution at the various impact bead positions and found that the optimum bead position possessed maximum aerosol density which was not of minimum droplet size. As a result, increased solute volatilisation interferences such as the maximum suppression of calcium by phosphate, occurred at the optimum position of the impact bead. The increased fluctuation of the absorbance on the gradient of the absorbance-bead displacement curve in Fig. 2.6 would be due to the wide range of aerosol droplet-sizes that vaporised to produce atoms at different rates in the flame. Studies on solute volatilisation interferences are presented in the next three chapters.

The adjustment of the nebuliser capillary tip in its venturi nozzle offered a 30% increase over the optimum absorbance of magnesium by the impact bead adjustment. The capillary tip at the manufacturer's setting was 2 mm out of its housing and the maximum absorbance occurred when the capillary tip receded 0.4 mm into its
Although the liquid uptake rate increased as the capillary tip receded, the maximum uptake rate occurred after the maximum absorbance, at a further withdrawal of the tip into its housing. The aspirating gas flow rate increased as the tip receded till it bubbled out of the test solution through the capillary tube. The trend of increase in absorbance, aspirating gas flow rate and the liquid uptake rate agreed with the work of Howarth and coworkers\textsuperscript{5} except that the maximum absorbance occurred at reduced liquid uptake prior to the maximum suction. The increased absorbance was with increased aerosol density of large droplet sizes hence the fluctuation in the absorbances increased from 1\% to 2\% of signals. The increased aerosol density eventually overloaded the flame at higher uptake rates to cause a fall in the flame temperature, and an increase in solute volatilisation interferences.\textsuperscript{10} However, Sturman used this region of the capillary tip adjustment to offer maximum suction/liquid uptake and so minimised the effects of hydrostatic head variation that would normally occur when samples are aspirated conventionally.

The adjustments of the capillary tip, while the air flow rate was maintained constant, caused the nebuliser liquid uptake rate to increase to a plateau. The uptake rate then decreased sharply to level off as the capillary tip was withdrawn well within its housing (see Fig. 2.9.(i)). The absorbance, however, decreased gradually and resonated as the capillary tip was withdrawn into its housing. The absorbance resonation could be a reflection of a defect in the concentricity of the capillary tip in the venturi-nozzle of the Baird nebuliser. Hence the trends of results are more reliable than the absolute values for the experiments involving variation in the capillary tip position in this and other related chapters of this thesis.

**Controlled flow/FIA**_ The use of an external pump to deliver solutions to the nebuliser offers a more precise control of the nebuliser uptake rate, independent of the nebuliser gas or length of the attached capillary tube.\textsuperscript{83,84} In the experiments, the steady state and the FI- absorbances of magnesium decreased as the pumping flow rate decreased (see Figs. 2.13 and 2.16.(i)). The absorbances decreased as the pumping rate decreased because of the reduced analyte mass transport to the nebuliser. The decrement, however, was increasingly reduced as the pumping flow rate decreased because of increased nebuliser transport efficiency. The FI-absorbance curve passed through a maximum instead of levelling off because the spectrometer's response electronics could not follow the fast transient signals that occurred at high flow rates. The large sample volumes required for steady state absorbances overshadowed this effect hence the steady state absorbance curve
levelled off at high pumping flow rates. These observations agree with the general behaviour of AA spectrometers as reported by workers such as Cresser, Stewart, Tyson and their coworkers.\textsuperscript{50,53,85}

The fluctuations of the steady state absorbances worsened from 2\% of the signal at \( \geq 5 \text{ ml min}^{-1} \) to 20-30\% at \(< 1 \text{ ml min}^{-1} \) (see Fig. 2.16.(i)). The fluctuations in the absorbances were observed as oscillations on the absorbance-time response profiles of both FI- and steady state absorbances. The effect seems to support the suggestion of Garcia and coworkers that the slow pulsations of the peristaltic pump caused a premature break-up of the liquid thread at nebulisation.\textsuperscript{50} The oscillations on the transient peaks collapsed to produce sharp reproducible peaks when the speed of the chart recorder was increased. Hence the precision of the FI-peak heights (on the average, 2 \% RSD for all flow rates as shown in Table 2.6) was not significantly affected when flow rates were varied. However, the pulsations caused the dilution factors to be increasingly higher than expected at flow rates of less than 3 ml min\(^{-1}\). Hence precoils are either insufficient or ineffective pulse dampers for the peristaltic pump especially at low flow rates. It is not surprising then that the minimum fluctuation in the steady state absorbances was 2.5 - 3\% of signal at 4 - 7 ml min\(^{-1}\) and it was not significantly changed when the nebuliser capillary tip was adjusted (see Table 2.5). The steady state fluctuations were a factor of two to three worse in comparison with the noise from conventional aspiration by the adjustment of the capillary tip or tube length. Despite the demerit of the peristaltic pumping, it offered more consistent liquid flow rates and higher absorbances at \( \geq 7 \text{ ml min}^{-1} \) than conventional aspiration (see Fig. 2.14). Therefore one may infer that FIA could offer higher sensitivity than conventional aspiration as already observed by Ruzicka, Fang and their coworkers.\textsuperscript{83,86} But the high flow rate needed is in the flow regime where the response of a spectrometer's recording electronics could sometimes obscure the effect.

The FI- absorbance of magnesium increased non-linearly as the injected sample volume increased to attain finally the steady state (see Fig. 2.16.(ii)). The associated dilution factors decreased as a mirror image of the absorbance curve to attain finally the value 1. In an opposite trend, absorbance decreased as the length of tube traversed by the sample plug increased and the associated dilution factor increased linearly for about 2 meters before levelling. These results have trends similar to the works of Tyson and his group,\textsuperscript{33,35,85,87,88} which were carried out at Loughborough University. The interpretation of the results and the implications for the AAS as a non-ideal FI- detector (with a behaviour similar to one or more mixing
tanks) have been well treated in the works of Stone\textsuperscript{87} and Appleton\textsuperscript{35}.

FI- flame AAS minimised the effects of high dissolved solids and of sample viscosity in agreement with the reports of Fang, Tyson, Zhou and their coworkers\textsuperscript{85,89,90,91} (see Figs. 2.17 and 2.18). The improvement was best at high flow rates where the transient nature of the signals and the high ratio of the wash-to-sample residence times prevented the blockage of the nebuliser or burner. The present work shows the importance of the manifold dilution factor in the quantitation of samples with high dissolved solids or viscosity. The high dilution factor of 5 offered a plateau region in the absorbance-matrix content curve which would favour sample analysis without matrix matching. Although sensitivity was reduced at the dilution factor of 5, the precision of peaks, at roughly 1\% RSD, was improved two-fold over lower dilutions.

2.6. CONCLUSIONS

For conventional aspiration of the nebuliser, the liquid uptake rate, absorbance and nebulising gas flow rate vary concurrently on adjustment of the nebuliser capillary tip in its nozzle. The adjustment of the capillary tip could offer high absorbance at high flow rates and, in some adjusted positions, exhibited increased noise level. The capillary tip position of maximum sensitivity differs from that of maximum liquid uptake rate. A precise control of the capillary tip would be required for the adjustments to offer reproducible results.

The use of an external pump offered consistent control of nebuliser liquid uptake rate without offsetting the nebulising gas flow. However, the pulsations of peristaltic pumping caused the fluctuations of steady state absorbance to increase especially at low liquid flows. Precoils are either insufficient or ineffective pulse dampers especially at low flow rates. The adjustment of nebuliser capillary tip affected absorbance sensitivity and not absorbance fluctuations.

Flow injection-flame AAS, using the peristaltic pump, offered precision which was not significantly different from that of conventional aspiration. Flow injection-flame AAS could offer higher sensitivity than conventional aspiration only at very high flow rates and only if the time constant of the spectrometer can cope with transient signals.
REFERENCES

CHAPTER THREE

REMOVAL OF SOLUTE VOLATILISATION INTERFERENCES IN CALCIUM DETERMINATION

3.1. INTRODUCTION

The depressive effects of anionic species such as aluminate, phosphate and silicate on the absorbance of calcium in the air-acetylene flame are well documented.1-9 The effects are classified as solute volatilisation interferences because the refractory compounds formed from the solution matrix on evaporation in the flame, do not readily yield free vapour phase atoms of calcium. The decreased concentration of free calcium atoms in the spectrometer’s light-path produce lower absorbance than those of simple calcium solutions. The literature reports1,2,6 showed the following two categories of such interferences for calcium: (a), the absorbance of calcium decreased as the concentration of phosphate increased and the absorbance finally levelled off at high concentrations of the interferent; and (b), the absorbance of calcium decreased continuously as the concentration of the interferent increased for calcium/aluminium and calcium/silicate systems.

The mechanism of calcium/phosphate interference has been commonly studied. The reports of workers such as Rubeska and Moldan1 as well as Long and coworkers8 show the formation of refractory compounds to proceed if a particular element in the aerosol particle occurred as an oxide. In addition, Long and coworkers7,8 as well as Saito and coworkers9 showed that phosphine, one of the normal contaminants of acetylene fuel, depressed the absorbance of calcium in air- and nitrous oxide-acetylene flames. This calcium/phosphine interference was caused by the reaction between the combustion products of phosphine and aerosol particles which formed a slow vaporising (refractory) compound similarly to the effect encountered with the calcium/phosphate interference.8 Therefore methods of controlling these interferences have aimed at preventing the formation of refractory compounds by the adjustments of nebuliser-burner parameters and by the use of additional solution chemistries as follows:

Suitable adjustment of the instrument parameters such as the flow spoilers in the nebuliser,15 could generate aerosol droplet distribution of small mean size which in turn desolvate to generate small sized aerosol particles. Additional adjustment of the burner height and fuel-oxidant ratio or fuel type7,16 all aid the
vaporisation and atomisation of the aerosol particles in the flame. However, these adjustments often sacrifice sensitivity and have little effect on the severe depression caused by aluminium.\textsuperscript{1,6}

Addition of a large excess of a releasing agent (such as lanthanum or strontium ions) or a protective chelating agent (such as EDTA) to the aspirated solutions causes vapour-phase reactions which leave the calcium atoms free. A high solute concentration that could result from these additions, however, increases the possibilities of clogging in the nebuliser and the burner. A high solute content could also cause an aerosol ionic redistribution to occur,\textsuperscript{17} in which case, the nebuliser-impactor sampling would generate an aerosol of different concentration of calcium ions for the flame.

Also, traces of calcium have been isolated from its interferents by coprecipitation with ferric hydroxide\textsuperscript{18} or extraction with the naphthenate solution\textsuperscript{19} prior to nebulisation. Such separation procedures not only prolong the analysis but could introduce contamination. Hence the results are never as accurate as the direct analysis of simple calcium solutions.

Typically, analysis of calcium in real samples such as biological fluids, agricultural products, metal ores and alloys\textsuperscript{10,11} has often possessed systematic errors because of some failure of the traditional methods of controlling interferences.\textsuperscript{12-14}

Flow injection- flame AAS has been applied to extend the performance of the atomic spectrometer as well as to improve upon existing analytical procedures. The reports of many workers on the presentation and dilution of samples with high concentration of dissolved solids, modification of samples, particularly by the removal of interferents, and fast interpolative calibrations have been presented in section 1.3.

Thus, calcium has been determined in several interferent media by FI- flame AAS without the addition of releasing agents as follows:

(a), Tyson and Idris\textsuperscript{20,21} effected the method of standard additions in a single line manifold to control the calcium/phosphate interference. However, the calcium/aluminium interference that does not possess a saturation level still required the addition of a releasing agent for accurate analysis.

(b), Kamson and Townshend\textsuperscript{22} used an on-line ion-exchanger to remove the effects of phosphate and sulphate but not aluminium.

(c), Martinez-Jimenez and coworkers\textsuperscript{23} precipitated calcium as the oxalate to remove the effects of sulphate, molybdate, iodate and arsenate. And

(d), the benefits of starvation conditions for increasing nebulisation efficiency have
been used to remove phosphate effects, with the claim that air-compensation additionally enhanced the peak height signal for calcium.\textsuperscript{24,25}

The latter reports, contained in (c) and (d), have exemplified the removal of phosphates and omitted the severe effects of aluminium. Therefore, in this chapter, studies on the adjustments of both AA instrument parameters, as well as the physical parameters of a single line manifold are reported for the removal of phosphate and aluminium effects on calcium. In addition, the effects of organic solvents, air-compensation and air-pulse damper on the FI-absorbance of calcium are reported.

3.2. APPARATUS AND REAGENTS

The single line manifolds used for FIA are shown in Fig. 3.1. These manifolds were constructed from PTFE tubing, i.d., 0.58 mm. The peristaltic pump was a Gilson Minipuls-2 furnished with PVC tubing, i.d., 2.79 mm, to offer high flow

![Fig. 3.1. Single line manifolds used for the study of phosphate and aluminium interferences on calcium. (Pc, precoil; Ps, pulse damper, I, injection port; S, sample loop; a, air compensation inlet; and AAS, spectrometer.)]
rates up to 10 ml min$^{-1}$. The pump tube was later changed to a PVC tube, of smaller i.d., 1.6 mm, which offered low flow rates of 0 - 4 ml min$^{-1}$. The air compensation inlet was a PTFE tube, i.d., 0.58 mm, and 3 cm long, connected to the arm of an omnifit T-piece. The injection valve, the air-column pulse damper and the precoil have been described in section 2.2. The atomic absorption spectrometer, Baird-Atomic, Model A3400, was connected to a Philips AR55 chart recorder for absorbance measurements or otherwise connected to a Baird-Atomic Datacomp microprocessor for area integration measurements. The nebulising gas was supplied by an air compressor.

Calcium solutions were prepared by diluting stock 1000 mg l$^{-1}$ solutions (BDH Spectrosol grade). Orthophosphoric acid (Arista, 85% pure, having maximum calcium impurity of about 2 mg l$^{-1}$) and aluminium chloride (reagent grade, minimum assay 97%) were used as interferents. Ammonia, ethanol and n-hexane were all BDH AnalaR compounds. Reagent grade water (LiquiPure RG system; reverse osmosis followed by ion-exchange) was used for making up the solutions and for carrier stream.

3.3. PROCEDURES AND RESULTS

3.3.1. Optimisation of Baird-Atomic (A3400) spectrometer

The manufacturer's absorption performance data for calcium were used to start the operation of the spectrometer. The wavelength control was tuned slowly from 422 to 424 nm to offer minimum absorbance at 423 nm on the wavelength meter. Further optimisation procedures for the determination of calcium at maximum sensitivity were carried out in a manner similar to the optimisation of magnesium as reported in section 2.4. Figure 3.2 shows the results of the adjustments of the flame composition, burner height and lamp current. The optimum conditions afforded by the adjustments are shown in Table 3.1. These conditions were chosen to give maximum sensitivity as well as minimum absorbance noise for calcium determination.
Fig. 3.2. Effect of instrument parameters on the absorbance of 10 mg t\(^1\) Ca.
(i), acetylene flow at air flow rate, 7.5 l min\(^{-1}\);
(ii), burner position at air + acetylene flows, [7.5 + 3] l min\(^{-1}\);
(iii), lamp current at air + acetylene flows, [7.5 + 3] l min\(^{-1}\) and burner height, 2.5 cm.
Table 3.1. Optimum conditions for calcium on Baird-Atomic, Model A3400, spectrometer

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength, nm</td>
<td>422.7</td>
</tr>
<tr>
<td>Slit width, nm</td>
<td>0.5</td>
</tr>
<tr>
<td>Lamp current, mA</td>
<td>5.9</td>
</tr>
<tr>
<td>Supporting gas/flow rate, 1 min^-1</td>
<td>Air/7.5</td>
</tr>
<tr>
<td>Fuel gas/flow rate, 1 min^-1</td>
<td>Acetylene/3.0</td>
</tr>
<tr>
<td>Burner height, cm</td>
<td>2.5</td>
</tr>
<tr>
<td>Read out</td>
<td>Direct</td>
</tr>
<tr>
<td>Scale expansion</td>
<td>1</td>
</tr>
<tr>
<td>Curve correction</td>
<td>Linear</td>
</tr>
<tr>
<td>Damping</td>
<td>Off</td>
</tr>
<tr>
<td>Impact bead</td>
<td>Optimum*</td>
</tr>
<tr>
<td>Capillary tip adjustment</td>
<td>About 0.5 mm into its housing.</td>
</tr>
</tbody>
</table>

* Manufacturer's reference, impact bead close to the venturi nozzle.

The spectrometer was set with the optimum conditions shown in Table 3.1 and a normal calibration procedure was carried out with the six standard solutions of calcium shown in Table 3.2. The normal curve for calcium, shown in Fig. 3.3, was concave towards the concentration axis. A tangent drawn to pass through the linear portion (0 - 2 mg l^-1) of the curve offered a slope/sensitivity of 0.055. This sensitivity corresponds to a characteristic concentration of 0.08 mg l^-1. This experimental value for characteristic concentration was poor compared with the value, 0.05 mg l^-1/0.0044 abs., stated for calcium in the Baird-atomic, Model A3400, instrument manual. A discrepancy could arise if the manufacturer opted for the instrumental adjustments that afforded maximum sensitivity irrespective of the signal noise. Figure 3.2.(iii) shows that the best lamp current for the determination of calcium is a compromise between sensitivity and absorbance fluctuations. The implication is that a calibration slope/sensitivity better than 0.055 could be obtained at a lower lamp current than 5.9 mA but it would be with increased signal noise. This effect was investigated further. The normal calibration of the spectrometer was carried out for calcium at various lamp current and fuel flow combinations. The results are shown in Fig. 3.4.
Table 3.2. Absorbance readings of the standard solutions of calcium at conventional aspirations of the optimised, Baird-Atomic, Model A3400, spectrometer

<table>
<thead>
<tr>
<th>solution</th>
<th>concentration, mg \text{l}^{-1}</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>0.000 ± 0.002</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>0.060 ± 0.002</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>0.110 ± 0.002</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>0.240 ± 0.005</td>
</tr>
<tr>
<td>5</td>
<td>7.0</td>
<td>0.320 ± 0.005</td>
</tr>
<tr>
<td>6</td>
<td>10.0</td>
<td>0.430 ± 0.005</td>
</tr>
<tr>
<td>7</td>
<td>20.0</td>
<td>0.730 ± 0.005</td>
</tr>
</tbody>
</table>

Fig. 3.3. Normal working curve for calcium at 422.7 nm, spectrometer set for maximum sensitivity.
Fig. 3.4. Variation of the linear range of normal working curve for calcium at 422.7 nm for different lamp currents and acetylene flow rates: (i), 5.0 mA; (ii), 5.9 mA; and (iii), 7.0 mA.

(acetylene flows, 1 min⁻¹: 2.5 (●); 3.0 (○); 3.5 (□); 4.0 (●); and the other instrument parameters are optimum.)
All the normal calibration curves, with the exception of one, could be fitted with second-order polynomials of minimal residual errors. However the curvature was least pronounced for the optimum acetylene flow of 3.01 min\(^{-1}\), whatever the lamp current. The linear range of 0 - 2 mg l\(^{-1}\) was common to all the curves and a useful linear range of 0 - 7 mg l\(^{-1}\) occurred only at the high lamp current of 7 mA (see Fig. 3.4.(iii)). A tangent drawn to pass through the linear range, for each curve, offered increased slope/sensitivity as the lamp current decreased. This experiment shows that the instrument conditions that afford the best useful linear range may not necessarily afford maximum sensitivity.

The calibration curve having the best useful linear range possessed a point of inflection. This could be an indication that a three-dimensional plot of absorbance, lamp current and acetylene flow for calcium would exhibit multiple maxima. The validity of the multiple maxima phenomenon would, however, require further experiments, designed so as to enable the collection of a large number of calibration data. Such an experiment is best carried out with a computer facility which was not planned for the present work.

### 3.3.2. Interference effect of phosphate on calcium absorbance

The effect of phosphate on the absorbance of calcium was studied. The spectrometer was operated at the optimum conditions shown in Table 3.1. The nebuliser liquid uptake with these conditions was 8.0 ml min\(^{-1}\). The manifold shown in Fig. 3.1.(i) was used for FI-studies. Eleven solutions, each containing 10 mg l\(^{-1}\) Ca with varied concentrations of orthophosphoric acid in the range 0 - 100 mg l\(^{-1}\), were used in the experiment. The solutions were injected into the water stream which was pumped at 6.2 ml min\(^{-1}\). Five replicate injections were carried out for each solution and similarly for the three blanks that contained 10, 100, and 1000 mg l\(^{-1}\) H\(_3\)PO\(_4\). The procedure was carried out at the manifold parameters that offered approximate dilution factors of 5, 2 and 1 as follows:

- 70 µl injection, through 229 cm tube (dilution factor 5);
- 70 µl injection, through 20 cm tube (dilution factor 2); and
- 170 µl injection, through 20 cm tube (dilution factor 1).

The absorbance peaks were recorded on a chart at a speed of 60 s cm\(^{-1}\). The mean peak heights of the absorbances were used for the plots shown in Fig. 3.5.

Absorbances of the solutions and the blanks were determined for the conventional aspiration of the nebuliser. Solutions that contained 5 mg l\(^{-1}\) Ca plus different
concentrations of orthophosphoric acid were aspirated conventionally, for their absorbance to be compared with those from FIA of approximate dilution factor of 2. In the experiment, the blanks produced no significant absorbance for both conventional aspiration and FIA.

![Graph](image)

**Fig. 3.5.** Interference curves of calcium/phosphate with the spectrometer set for maximum sensitivity of calcium determination. (i), test solutions having 10 mg l\(^{-1}\) Ca; and (ii), test solutions having 5 mg l\(^{-1}\) Ca. (normal nebulization (Δ); and FI- peaks at dilution factor of 1 (●), 2 (○) and 5 (◆).)
The calcium/phosphate interference curve exhibited an initial enhancement followed by a depression for both conventional aspiration and FIA. The phosphate depressed the absorbance of calcium to a constant level of about 23% of the absorbance of the simple calcium solution levelling off at the matrix concentration that had a phosphate to calcium ratio of 2 and above. Absorbance for the conventional aspiration of the solutions having 5 mg l⁻¹ Ca did not differ significantly from the FI- absorbance of the solutions having 10 mg l⁻¹ Ca, at the dilution factor of 2. This could be that FIA, at high pumping rates, alleviated the calcium/phosphate interference by a dilution effect. Therefore the effect of pumping flow rate on calcium/phosphate interference was studied (see section 3.3.3.).

3.3.3. Effect of pumping rate on the calcium/phosphate interference

The spectrometer was operated with the optimum conditions shown in Table 3.1 and connected to the manifold as shown in Fig. 3.1.(i). The volume of the sample loop was 70 μl and the length of the tube from the valve to the spectrometer was 20.0 cm. Five replicate injections were made for each sample at the pump meter settings that offered pumping flow rates from 0.45 to 11.8 ml min⁻¹. The peak heights were recorded on chart at 60 s cm⁻¹. Each solution was pumped through the manifold for the steady state absorbance which was also recorded on chart. The liquid flow rate at each pump setting was determined gravimetrically. The collated data were plotted as shown in Figs. 3.6 and 3.7.

The steady state and the FI- absorbances of calcium increased as the pumping flow rate decreased and reached maximum values at 3 - 4 ml min⁻¹ then the absorbances fell sharply to roughly 60% of the maximum values at pumping flow rates of 0.75 and 0.54 ml min⁻¹ respectively. The FIA and the steady state procedures removed the calcium/phosphate interference effect for low interferent to analyte concentration ratios as from pumping flow rates of < 2.5 ml min⁻¹. High interferent to analyte ratios were alleviated only at low pumping rates particularly with the steady state procedure.

The precision for both FIA and steady state were in the range of 2 - 6% RSD. The poor precision was due to the rapid change of absorbance with flow rate as well as the pronounced effect of the pump pulsations as the pumping rate decreased. However steady state offered more stable precision than FIA because the latter was additionally affected by the reproducibility of the sample injections. A further demerit of FIA was its throughput which decreased from ≤ 6 s per peak at greater
Fig. 3.6. Effect of pumping rate on the Fl- absorbance of calcium without air compensation and the spectrometer set for maximum sensitivity: (i), 10 mg l\(^{-1}\) Ca; and (ii), 5 mg l\(^{-1}\) Ca; with phosphate concentrations of (\(\bigstar\)) 0 mg l\(^{-1}\), (\(\bigstar\)) 20 mg l\(^{-1}\), and (\(\bigstar\)) 200 mg l\(^{-1}\).
Fig. 3.7. Effect of pumping rate on the steady state absorbance of calcium without air compensation and the spectrometer set for maximum sensitivity:
(i), 10 mg l\(^{-1}\) Ca; and (ii), 5 mg l\(^{-1}\) Ca; with phosphate concentrations of (□) 0 mg l\(^{-1}\), (●) 5 mg l\(^{-1}\), and (▲) 20 mg l\(^{-1}\).
than 3 ml min\(^{-1}\) to 60 s per peak at 0.75 ml min\(^{-1}\).

The effects of an air-column pulse damper and air-compensation on the absorbance of calcium at different pumping flow rates were studied. The manifold shown in Fig. 3.1.(ii) was used. The T-piece for the air-compensation was placed horizontal\(^{24,25}\) at 18.0 cm tube length from the valve and 4.0 cm from the spectrometer. Three replicate injections were carried out for each test solution at each pump setting. The data collection was in accordance with the operation manual of the Baird-Atomic microprocessor\(^{26}\) which was used to record the absorbance peak heights and peak areas. The concentration of the interferent was 200 mg l\(^{-1}\) phosphate because the previous experiment could not alleviate such interference even at very low pumping flow rates. The results are shown in Fig. 3.8.

The FI- procedure with air compensation possessed a lower sensitivity which was about 50 percent of the absorbances from the continuous streams at the same pumping rate. The effect of the phosphate was eliminated for the interferent to analyte concentration ratio of 4 for both 10 and 5 mg l\(^{-1}\) Ca, though the removal occurred at flow rates of less than 1.8 ml min\(^{-1}\) for the 10 mg l\(^{-1}\) Ca. The precision of the FI- peak heights (1 - 6% RSD) and peak areas (1 - 4% RSD) did not differ significantly from the precision obtained by continuous stream (2 - 6% RSD) except at flow rates of \leq 0.5\) ml min\(^{-1}\), where air-compensation seemed superior due to the effect of the pulse damper. The steady state absorbances for both air compensation and continuous streams were of similar sensitivity in this experiment and the effect of a high concentration of the interferent was alleviated only at flow rates of less than 0.5 ml min\(^{-1}\) for both methods. There was a discontinuity in the absorbance-flow rate curve for the peak height measurements in the air-compensation procedure. This could be due to the pronounced nebuliser suction effect and continuous air bubbles acting together to cause lower than expected absorbances. The nebuliser liquid uptake rate through this manifold, without the peristaltic pump, was determined and found to be 1.48 ml min\(^{-1}\). This value coincided with the value of pumped flow rate for the on-set of discontinuity. Hence the use of a pump tube of smaller i.d., than the 2.76 mm used in these experiments, may possibly eliminate such discontinuity. The FI- peak area curves had the merit of not exhibiting the discontinuity.
Fig. 3.8. Effect of pumping rate on the absorbance of calcium with air compensation and the spectrometer set for maximum sensitivity: (I), FI- peak height; (II), FI- peak area; and (III), steady state absorbances.

[() 10 mg l⁻¹ Ca, (া) 10 mg l⁻¹ Ca plus 200 mg l⁻¹ phosphate, (०) 5 mg l⁻¹ Ca, and (॰) 5 mg l⁻¹ Ca plus 200 mg l⁻¹ phosphate.]
3.3.4. Optimisation of the determination of calcium at minimum interference of phosphate

The spectrometer was operated at maximum sensitivity for the determination of calcium. The positions of the impact bead and the nebuliser capillary-tip were set at the manufacturer's recommended positions. The normal optimisation procedure was carried out and the aspirated solutions were 10 mg l\(^{-1}\) Ca, with and without 200 mg l\(^{-1}\) phosphate (an amount of interferent that would normally cause maximum depression of the absorbance of calcium). The results of the adjustments: (a), fuel oxidant ratio; (b), burner height; (c), lamp current; and (d), capillary tip; are shown as graphs in Fig. 3.9.

![Graph](image)

**Fig. 3.9.** Effect of instrument parameters on the absorbance of calcium. (i), acetylene flow at air flow rate, 7.5 l min\(^{-1}\); (ii), burner position at air + acetylene flows, [7.5 + 4] l min\(^{-1}\). (o) 10 mg l\(^{-1}\) Ca, (•) 10 mg l\(^{-1}\) Ca plus 200 mg l\(^{-1}\) phosphate. (chosen settings are shaded.)
Fig. 3.9. Effect of instrument parameters on the absorbance of calcium. 

(iii), lamp current at air + acetylene flows, \([7.5\, +\, 4] \, \text{I min}^{-1}\) and burner height, 1.0 cm; 
(iv), capillary tip adjustment at air + acetylene flows, 
\([7.5\, +\, 4] \, \text{I min}^{-1}\), burner height, 1.0 cm and lamp current, 6 mA: 
(●) 10 mg l\(^{-1}\) Ca, (○) 10 mg l\(^{-1}\) Ca plus 200 mg l\(^{-1}\) phosphate. 
{chosen settings are arrowed.}

The regions of minimum difference, as well as minimum fluctuation, in the absorbances of the test solutions were chosen as the final settings for the optimised spectrometer (see Table 3.3).

Normal calibration procedures for calcium were carried out and the standard solutions of calcium with and without the amount of phosphate that would have
caused maximum interference, were used. Two nebuliser capillary-tip positions that offered minimum depression in the optimisation procedure were chosen for the calibrations. The results are shown in Table 3.4 and Fig. 3.10.

Table 3.3. Optimum conditions for calcium with minimum phosphate interference on Baird-Atomic (A3400) spectrometer

| wavelength, nm | 422.7 |
| slit width, nm | 0.5 |
| lamp current, mA | 6.0 |
| supporting gas/flow rate, l min⁻¹ | air/7.5 |
| fuel gas/flow rate, l min⁻¹ | acetylene/4.0 |
| burner height, cm | 1.0 |
| read out | direct |
| scale expansion | 1 |
| curve correction | linear |
| damping | off |
| impact bead | optimum* |

* manufacturer's reference, bead set close to the venturi nozzle.

Table 3.4. Absorbance readings of the standard solutions of calcium with and without phosphate interferent.

(i), nebuliser capillary-tip displacement, 0 mm.

<table>
<thead>
<tr>
<th>solution</th>
<th>[Ca²⁺], mg l⁻¹</th>
<th>[PO₄³⁻]: 0 mg l⁻¹</th>
<th>200 mg l⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Absorbance</td>
<td>Absorbance</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>0.050 ± 0.002</td>
<td>0.058 ± 0.002</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>0.098 ± 0.002</td>
<td>0.105 ± 0.005</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>0.214 ± 0.005</td>
<td>0.230 ± 0.005</td>
</tr>
<tr>
<td>5</td>
<td>7.0</td>
<td>0.290 ± 0.005</td>
<td>0.300 ± 0.005</td>
</tr>
<tr>
<td>6</td>
<td>10.0</td>
<td>0.395 ± 0.005</td>
<td>0.405 ± 0.005</td>
</tr>
<tr>
<td>7</td>
<td>12.0</td>
<td>0.455 ± 0.005</td>
<td>0.460 ± 0.010</td>
</tr>
</tbody>
</table>
(ii), nebuliser capillary-tip displacement, 2.65 mm.

<table>
<thead>
<tr>
<th>solution</th>
<th>[Ca$^{2+}$], mg l$^{-1}$</th>
<th>[PO$_4^{3-}$]: 0 mg l$^{-1}$</th>
<th>Absorbance</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>Absorbance</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>0.052 ± 0.002</td>
<td>0.058 ± 0.002</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>0.130 ± 0.002</td>
<td>0.142 ± 0.002</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>0.295 ± 0.005</td>
<td>0.305 ± 0.005</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>7.0</td>
<td>0.390 ± 0.005</td>
<td>0.400 ± 0.005</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>10.0</td>
<td>0.520 ± 0.010</td>
<td>0.520 ± 0.010</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>12.0</td>
<td>0.580 ± 0.010</td>
<td>0.580 ± 0.010</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3.10. Normal calibration curves for calcium at 422.7 nm. The spectrometer was optimised for minimum phosphate interference.
(i), nebuliser capillary-tip was at 2.65 mm displacement for solutions with (•) and without (○) 200 mg l$^{-1}$ phosphate; and
(ii), nebuliser capillary-tip was at 0 mm displacement for solutions with (•) and without (○) 200 mg l$^{-1}$ phosphate.
The calibration graphs were curves with second-order polynomials as best fit. The curves exhibited linear range of 0 - 1 mg l\(^{-1}\) Ca irrespective of the position of the nebuliser capillary-tip. However, adjustment of the capillary tip within the region of minimum depression offered better sensitivity such that a 2.65 mm adjustment had a characteristic concentration of 0.055 mg l\(^{-1}\) Ca whereas unadjusted position offered 0.08 - 0.09 mg l\(^{-1}\)/0.0044 abs. The increased sensitivity was disadvantaged by increased absorbance noise.

The calibration curves, with and without interferent, were within each others' limits of absorbance fluctuations at a given capillary tip adjustment. Hence the feasibility of using the optimisation, for minimum interference of calcium, without further matrix modification was studied further in section 3.3.5. The experiment for this study was designed to check that the depression of absorbance was removed for 10 mg l\(^{-1}\) Ca in a series of solutions having up to 2000 mg l\(^{-1}\) phosphate.

3.3.5. Effect of phosphate on the absorbance of calcium with spectrometer set for minimum phosphate interference

The spectrometer was operated at the conditions for minimum interference as set out in Table 3.3. The test solutions contained different amounts of the interferent in the range 0 - 2000 mg l\(^{-1}\) phosphate. The solutions were aspirated conventionally at the manufacturer's capillary-tip adjustment and at a further adjustment that offered increased liquid uptake rate and sensitivity. The spectrometer was then connected to the manifold as shown in Fig. 3.1.(ii) for FI- studies. The FI- pumping was carried out, with and without air compensation, at the two capillary-tip positions. Five replicate 70 µl injections, were made through [18 cm + 4 cm] tube length (the T- piece for air compensation was 18 cm from the injection port and 4 cm from the nebuliser) for each data condition. All absorbances were recorded as peak heights at a chart speed of 60 s cm\(^{-1}\). The average of the absorbance for each data, was used in the plots of the results shown in Fig. 3.11.

The interference curve for calcium at conventional aspiration, started with a slight depression of the calcium absorbance at below 5 mg l\(^{-1}\) phosphate. An enhancement of 1 - 9 percent of the absorbance of simple calcium solution occurred as from 5 mg l\(^{-1}\) phosphate and above. The enhancement is contrary to the depression observed when the spectrometer was set for maximum sensitivity of calcium in section 3.3.2. There was a region in the nebuliser capillary-tip positions where the adjustment of the capillary-tip affected the interference trend only to offer high
Fig. 3.11. Interference curves for 10 mg l\(^{-1}\) calcium with the spectrometer optimised for minimum phosphate interference at capillary-tip adjustments of (A), 0 mm; and (B), 2.65 mm. 

(●), conventional aspiration; FIA with (—), and without (—). 

air-compensation at the pumping flow rates of (● ●), 1.8 ml min\(^{-1}\) and (∆ ∆), 0.4 ml min\(^{-1}\).
sensitivity as the nebuliser liquid uptake rate was increased. Therefore, the analysis of calcium by conventional aspiration, would not require the addition of releasing agents to offer high sensitivity if the spectrometer is optimised for minimum phosphate interference. However, the solutions would have to contain an interferent to analyte concentration ratio $\geq 2$ for consistent results.

Flow injection methods, with or without air compensation, reduced the interference enhancement as the pumping flow rate decreased but the initial depression remained. In addition, air compensation offered lower sensitivities than the continuous streams for similar pumping flow rates irrespective of the capillary-tip position. The exception occurred only at very low pumping rates ($\leq 0.4 \text{ ml min}^{-1}$) within the region where peak height quantification did not reflect increased nebulisation efficiencies for this manifold design (see Fig. 3.8.1).

The precision of the results for both air compensation and continuous streams were similar in the experiments. However continuous streams frequently produced peaks with a sudden upsurge in absorbance due to the release of built-up air bubbles in the manifold. Such peaks were readily recognised on the chart recordings and were considered outliers. Air compensation eliminated the air-bubble effect which was particularly troublesome when the manifold was operated at pumping flow rates below the conventional aspiration of the nebuliser. Therefore, air compensation was applied in those studies of this research which involved low pumping rates so as to afford improved precision of peak height absorbance.

3.4. DISCUSSION

The absorbance of calcium was much affected by the fuel-oxidant ratio and the observation height in the flame. Phosphate affected the absorbance of calcium such that the absorbance maximum for the flame profile shifted towards a higher fuel composition (see Fig. 3.9). The consequence was that the normal optimisation conditions for maximum sensitivity of calcium required an adjustment to fuel-rich regions to minimise the effect of phosphate. These observations agree with the works of several authors such as Ulrich and Ramirez-Munoz, Maitra and Patsalides, and Garcia and coworkers. Ramirez-Munoz, in line with tradition, added releasing agents for the complete removal of phosphate interference as well as for the improved sensitivity of the calcium determination. Garcia and coworkers, however, applied flow injection techniques at the carrier flow rate of less than 0.2
ml min\(^{-1}\) for the complete removal of phosphate interference apparently with no loss in sensitivity for 10 mg l\(^{-1}\) Ca (see figures 3 and 4 of reference 24). In the present work, the application of FIA at low pumping rate removed the phosphate interference but it decreased the sensitivity and prolonged the analysis so that a carefully optimised spectrometer for minimum phosphate interference at conventional aspirations provided a better alternative (see Fig. 3.8 and Fig. 3.11). The phosphate depression was eliminated without sacrificing sensitivity. The adjustment of the nebuliser capillary tip was the crucial factor, in addition to the conditions of fuel composition and flame observation height. The adjustment of the capillary tip, when the spectrometer was set for minimum phosphate interference, did not significantly affect the signal noise. The effect could be due to the low uptake rate, 2.6 ml min\(^{-1}\) unadjusted and 3.8 ml min\(^{-1}\) at position of maximum sensitivity such that the nebuliser appeared to have produced more droplets of small mean size distribution with no significant increase in drop-size range. The distribution would then produce the increased sensitivity without increased signal noise. These characteristics are an additional advantage of the designed conventional procedure over FIA in the removal of phosphate interference.

The interference curve for calcium/phosphate, at conventional aspirations of the spectrometer which were optimised for maximum sensitivity, shows a slight enhancement at less than 20 mg l\(^{-1}\) phosphate and a major constant depression at 20 mg l\(^{-1}\) and above (see Fig. 3.5 and Fig. 3.11). Garcia and coworkers\(^{25}\) applied FIA with air compensation to eliminate the depressive effect of 0.01 mol l\(^{-1}\) (roughly 1000 mg l\(^{-1}\)) phosphate on 10 mg l\(^{-1}\) Ca. The authors used 35 \(\mu l\) injections of the test solutions at a carrier flow rate of 1.8 ml min\(^{-1}\) with the nebuliser previously set for conventional liquid uptake rate of 8 ml min\(^{-1}\). This work supports the findings of Garcia and coworkers\(^{25}\) for the phosphate depression was completely removed for 75 \(\mu l\) injections of 10 mg l\(^{-1}\) Ca plus 200 mg l\(^{-1}\) phosphate at carrier flow rates \(\leq 2 \text{ ml min}^{-1}\) (the nebuliser liquid uptake at conventional aspiration was 7 ml min\(^{-1}\)). Both phosphate concentrations are already on the constant depression level of the calcium/phosphate interference curve. The presented experiments in this work could not prove the literature claims\(^{25,28}\) that air compensation alleviated interference due to improved nebulisation efficiencies and decreased range of aerosol drop size than continuous streams. Air compensation exhibited lower peak height sensitivities than continuous streams for similar carrier flow rate and other FIA parameters (see Fig. 3.11). Hence air compensation appeared to aid the mixing/dilution processes in the sample bolus more than continuous streams. The dilution effect could also explain why air compensation alleviated phosphate
interference better for small injection volumes than large sample volumes that produced steady state absorbance (see Fig. 3.8 (I) and (II)). Fang and Welz, in a recent report, showed that the reduction of the interference of phosphate on calcium absorbance in the flow injection mode was due to the dilution effect as well as nebulisation efficiency. Therefore one might conclude that a nebuliser system that does not provide a high and rapid increase in nebulisation efficiency as the liquid uptake decreased, could cause the manifold dilution effect to be more operative. Such an effect would explain the reduced sensitivity of calcium for FIA with air compensation and for large injection volumes in the phosphate interference study as observed in the present work.

3.5. ALUMINIUM INTERFERENCE ON CALCIUM

3.5.1. Effect of Instrument parameters

The procedures used for the study of the interference of phosphate on calcium were carried out similarly for the study of calcium/ aluminium interference. The interference of aluminium on the absorbance of 10 mg l\(^{-1}\) calcium is shown in Fig. 3.12. The interference curve had an initial enhancement at low concentrations (about 10% at 1 mg l\(^{-1}\) Al), then a large depression at high concentrations (about 70% at 20 mg l\(^{-1}\)) and an almost complete suppression by 50 mg l\(^{-1}\) aluminium. The application of FIA, in which 70 μl injections were made through (18 + 4) cm tube length (the T-piece for air compensation was 18 cm from the injection port and 4 cm from the nebuliser), had no significant effect on the interference curve. Similarly the instrumental conditions for minimum interference of aluminium (chosen such that the absorbance difference between the aspirated solutions of calcium: 10 mg l\(^{-1}\) Ca; and 10 mg l\(^{-1}\) Ca plus 10 mg l\(^{-1}\) aluminium; was minimum (see Fig. 3.13 and Table 3.5), had no significant effect on the interference curve except to reduce the peak height sensitivity. In this case, the adjustment of the nebuliser capillary tip appeared to have negligible effect on the absorbance of calcium in the presence of aluminium. Therefore all subsequent experiments on the calcium/ aluminium interference were carried out with the spectrometer operated at the conditions of maximum sensitivity for calcium.
Fig. 3.12. Interference curves for 10 mg l\(^{-1}\) Ca. Spectrometer optimised for:
(A) maximum sensitivity of calcium; and (B) minimum aluminium interference.

(*) conventional aspiration; FIA with (---) and without (---), air-compensation at the pumping flow rates of (\oplus \circ), 3 ml min\(^{-1}\) and (\Delta \bullet), 0.4 ml min\(^{-1}\).
Fig. 3.13. Effect of instrument parameters on the absorbance of calcium:
(i), acetylene flow at air flow rate, 7.5 l min⁻¹;
(ii), burner position at air + acetylene flows, [7.5 + 4.5] l min⁻¹;
(iii), capillary tip adjustment at air + acetylene flows, [7.5 + 4.5]
1 min⁻¹, burner height, 3 cm and lamp current, 2.2 mA.
(①), 10 mg l⁻¹ Ca; (②), 10 mg l⁻¹ Ca plus 1 mg l⁻¹ aluminium; and
(③), 10 mg l⁻¹ Ca plus 10 mg l⁻¹ aluminium.)
Table 3.5. Optimum conditions for the interference of aluminium on the absorbance of calcium using the Baird-Atomic (A3400) spectrometer

<table>
<thead>
<tr>
<th>Maximum absorbance for difference for Ca with</th>
<th>Minimum absorbance for 10 mg l⁻¹ aluminium</th>
</tr>
</thead>
<tbody>
<tr>
<td>wavelength, nm</td>
<td>422.7</td>
</tr>
<tr>
<td>slit width, nm</td>
<td>0.5</td>
</tr>
<tr>
<td>lamp current, mA</td>
<td>2.2</td>
</tr>
<tr>
<td>air flow rate, l min⁻¹</td>
<td>7.5</td>
</tr>
<tr>
<td>acetylene flow rate, l min⁻¹</td>
<td>3.5</td>
</tr>
<tr>
<td>burner height, cm</td>
<td>0.5</td>
</tr>
<tr>
<td>read out</td>
<td>direct</td>
</tr>
<tr>
<td>scale expansion</td>
<td>1</td>
</tr>
<tr>
<td>curve correction</td>
<td>linear</td>
</tr>
<tr>
<td>damping</td>
<td>off</td>
</tr>
<tr>
<td>impact bead *</td>
<td>optimum</td>
</tr>
</tbody>
</table>

* manufacturer’s reference, bead set close to the venturi nozzle.

3.5.2. Effect of organic solvents in a single line manifold

Organic solvents such as ethanol, butanol and acetone have been used, in the literature, to increase nebuliser transport efficiency which in turn enhanced the peak height absorbance in the determination of metals. The determination of Cu and Zn has already been reported in chapter one, Section 1.3 of this report. Therefore the experiment that follows was designed so that a suitable choice of an organic solvent with or without flow compensation in FIA, might remove the depression due to calcium/aluminium interference.

The effect of organic solvents such as ethanol and n-hexane on the absorbance of calcium in the presence of aluminium was studied. The manifold shown in Fig. 3.1.(ii) was used. The nebuliser was operated conventionally to draw liquid at 8 ml min⁻¹. The water carrier stream was pumped at a low flow rate (1 ml min⁻¹). The test solutions were 10 mg l⁻¹ Ca plus aluminium in the concentration range.
of 0 - 30 mg l\(^{-1}\) and 38 µl of each solution were injected in triplicates into the carrier stream, through a 11 cm tube length to the nebuliser. The flow compensation was effected with a T-piece 7 cm from the injection port and 4 cm from the nebuliser. The results showed air and ethanol compensations to have similar effects which offered higher sensitivity than either water or n-hexane compensation (see Fig. 3.14.(A)). The compensation with n-hexane was of intermediate sensitivity, for

![Graph](image)

**Fig. 3.14.** Effect of organic solvents on the absorbance of 10 mg l\(^{-1}\) Ca. (A), 38 µl injections into water carrier through [7 + 4] cm tube length at 1.0 ml min\(^{-1}\); (o) air, (●) water, (+) ethanol and (●) n-hexane compensation; (B), 38 µl injections into (o), water; and (+), ethanol carriers with air compensation and through [7 + 4] cm tube length at 0.4 ml min\(^{-1}\).
reasons that could not be clearly defined due to its being immiscible with water or to its volatility. Perhaps its higher burning velocity reduced the residence time of the atoms in the spectrometer’s light path. This was evident for acetone, ethyl acetate and chloroform which caused the flame to lift from the burner head and so they were considered unsuitable for this experimental design. On the other hand, methanol and propan-2-ol behaved similarly to ethanol compensation. However, the aluminium interference was not removed even with the use of ethanol as the carrier stream which was pumped at 0.4 ml min\(^{-1}\) (see Fig. 3.14.(B)).

3.5.3. Discussion

The interference of aluminium on the absorbance of calcium was a continuous depression without a constant level. This observation agreed with results reported by previous workers\(^{1,5,12,21}\). The adjustment of the acetylene flame to fuel rich conditions reduced the sensitivity of calcium and had no significant effect on the depression caused by aluminium. Therefore aluminium forms a nonvolatile compound with calcium that could only increase its vapour-phase calcium atoms at high temperatures offered by fuel lean conditions or hotter flames such as the nitrous oxide- acetylene flame.

The application of FIA at the low pumping rates that normally offer increased nebulisation efficiencies for water and organic solvents\(^{32,33}\) could only reduce the depression for a similar reason. However certain inorganic compounds such as lanthanum chloride and potassium chloride, and organic compounds such as ammonium chloride, tetrabutyl-ammonium chloride and EDTA when present with aluminium have been reported to remove the depression of calcium absorbance\(^{1,5,34}\). These compounds, when present with calcium and aluminium in the desolvated particle, undergo explosive disintegrations to smaller particles on heating in the air-acetylene flame. The smaller particles so produced volatilise completely\(^{1,5}\). The process, however, was reported to require stoichiometric amounts of the compounds for the complete removal of the depression caused by aluminium. Therefore the removal of the aluminium interference depends more on flame chemistries and less on the efficiency of the nebuliser system.

3.6. CONCLUSIONS

The depressive effect of phosphate on calcium can be removed at low FI- pumping
rates that offer improved nebulisation efficiencies provided small injection volumes are used.

The flow injection procedure at low pumping rates reduced the sensitivity and prolonged the analysis so that the conventional aspiration with the operation of the spectrometer at the adjustments for minimum interference, provides a better alternative. In this respect, the adjustment of the nebuliser capillary tip relative to the nebulising gas outlet is of critical importance.

The depressive effect of aluminium on calcium cannot be removed by the sole adjustment of the physical parameters in either conventional and flow injection techniques.

Air and water compensations of the water stream in FIA are shown to have reduced sensitivity more than continuous streams. Air compensation was of higher sensitivity than water compensation for identical settings of flow-injection parameters and nebuliser liquid uptake rate. Polar organic solvents such as ethanol could be fed to the nebuliser with air compensation (without an auxiliary oxygen) to offer higher sensitivity than air compensated water stream.

Air compensation showed superior precision for the 'starved' nebuliser. The unpredictable occurrence of air bubbles in the flow stream caused a sudden upsurge of signals (measured as peak heights) in continuous streams but was of no significance in air compensated streams.

Air column dampers improved precision at low pumping rates, for the amplitude of the sinusoidal noise super-posed on the absorbance-time profiles was reduced.
REFERENCES


CHAPTER FOUR

ON-LINE PRECIPITATION IN FLOW INJECTION- FLAME
ATOMIC ABSORPTION SPECTROMETRY

4.1. INTRODUCTION

Precipitation reactions are applied for both analyte separation and enrichment in analytical chemistry as well as for quantitative determinations. The reactions, which include the formation of complexes, the formation of heteropolyacids and redox reactions, have been applied in flame atomic absorption spectrometry (FAAS) for the indirect determination of anions and organic compounds. These species are not usually determined directly by FAAS because the analyte elements in the species have their sensitive resonance lines in a part of the ultra-violet region of the electromagnetic spectrum inaccessible to routine determination. Such radiation is absorbed by other species generated by conventional flame spectrometers designed to function within the spectral range of 190 to 850 nm.

These indirect analytical procedures involve the formation of precipitates between the analyte species and a known quantity of a suitable metal ion, such as barium, silver or copper, which is easily measured by FAAS. The reaction should be quantitative and it may be necessary that the precipitates are separated from the reaction mixture by filtration, centrifugation or decantation. The concentration of excess metal ion in the filtrate or supernatant solution is determined by AAS. The concentration of the analyte is deduced from the difference between the initial and excess concentrations of the metal ion. An alternative approach is to dissolve the separated precipitate in a suitable solvent and the metal ion in the solution is subsequently determined by AAS. The concentration of the metal ion and the analyte species are, in this case, directly related. Precipitation reactions, including complexation and redox reactions, form the basis of indirect methods. These reactions have been applied to remove interferents and improve sensitivity in the FAAS of metal ions. Indirect methods, however, are rarely used in routine analysis because:

(a), they are time consuming;
(b), the nature of both the analyte and interferents have to be known for the reagents to be appropriately chosen;
(c), the reproducibility and accuracy of the methods depend on the efficiency of the
separations and could require a high degree of expertise;
(d) a considerable amount of laboratory glassware may be required such that the methods become cumbersome; and
(e) the methods are difficult to automate\textsuperscript{7-9} because they are multi-stage procedures.

Precipitation, being a solid-liquid heterogeneous reaction, is considered difficult to automate particularly in a continuous flow system. Firstly, the formation of fine particulates can clog the conduits or disturb the measurement of the analyte by the detector. Secondly, conditioning of a precipitate, needed for quantitative reaction and efficient separation, could be time-consuming. For example, the manual classical determination of oxalic acid in urine by the precipitation of calcium oxalate needed an hour to condition the precipitates as reported by Menache\textsuperscript{10} and a similar determination by Koehl and Abecassis\textsuperscript{11} required forty-eight hours. Difficulties notwithstanding, many workers such as Skinner and Docherty\textsuperscript{12} have devised ingenious procedures which resulted in the successful operation of continuous flow systems without the blockage of flow line components and conduits. The incorporation of ultrasonic devices in a flow-line was found to reduce drastically the time needed to condition the precipitates.\textsuperscript{13-15} The manifolds devised for on-line precipitations are used preferably for sample separations than for quantitative determinations. And detectors such as solution spectrophotometers are usually incorporated on-line to offer low running costs compared to FAAS.\textsuperscript{7} The removal of particulates from flow-streams were effected preferably by continuous filtration in chemistry whilst centrifugation is preferred in chemical engineering. Typically, the practice of continuous filtration used for solvent and sample cleaning is a common feature of automated process analysers and laboratory instruments for high performance chromatography (HPLC) and liquid chromatography (LC).\textsuperscript{16-18} The characteristics of the two main classes of filtration devices used for continuous filtrations are presented in Table 4.1. In practice, multi-stage filtration which incorporate coarse and fine filters are preferred. Such filtrations cause low pressure drop and therefore minimal change in the flow rate of these streams. Some filters are designed to be self-cleaning. Such filters are incorporated into the manifold so that the operating high flow rate of the liquid, in a bypass, sweeps off the particle deposits from the filter element in a back flush operation.

Continuous precipitations, carried out in flow-streams, segmented with air (SFA), were reported by Skinner and Docherty for the determination of potassium in fertilizers.\textsuperscript{12} The manifold was constructed as shown in Fig 4.1 and it has five
channels for the sample, reagents and air. The sample was mixed with excess of the reagent (sodium tetraphenylborate) and the precipitate (potassium tetraphenylborate) was filtered off continuously with a moving strip of Whatman no.4 filter paper. The absorbance of the reagent was monitored to afford the concentration of potassium by the method of measurements by difference. The sample was pretreated with a solution of formaldehyde to prevent the precipitation of the ammonium ion component of the fertilizer. An ultrasonic bath, fitted prior to the filter unit, was periodically actuated to prevent blockage of the conduits and a mixing chamber fitted

Table 4.1. Characteristics of the filter media used in sampling systems

<table>
<thead>
<tr>
<th>Filter-Type</th>
<th>depth (or cartridge)</th>
<th>membrane (or disc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i), fabrication:</td>
<td>sintered stainless steel, sintered ceramic, sintered organic polymers, and glass microfibre tubes.</td>
<td>sintered organic polymers such as PTFE, nylon, and cellulose; sintered inorganics such as alumina based compounds, carbon and glass microfibre paper</td>
</tr>
<tr>
<td>(ii), mechanical strength:</td>
<td>all fabrications are robust except ceramic and alumina based compounds.</td>
<td></td>
</tr>
<tr>
<td>(iii), pore-size:</td>
<td>wide range to 0.2 ( \mu \text{m} ) minimum size for all fabrications except steel which has 5 ( \mu \text{m} ) as minimum.</td>
<td></td>
</tr>
<tr>
<td>(iv), chemical strength:</td>
<td>PTFE can tolerate wide range of reagents; cellulose is intolerant except to water (pH = 7); ceramic and stainless steel are intolerant to bases and hydrofluoric acid respectively.</td>
<td></td>
</tr>
<tr>
<td>(v), operating temperature:</td>
<td>inorganic fabrications can withstand up to 550 - 800 °C; and organic fabrications can withstand up to 100 - 145 °C.</td>
<td></td>
</tr>
<tr>
<td>(vi), relative cost:</td>
<td>inorganic filters are more expensive.</td>
<td></td>
</tr>
</tbody>
</table>
prior to the spectrophotometric detector minimised the manifold dispersions and removed air bubbles. The manifold, though complex, was reported to offer accurate results. With the advent of FIA, such on-line precipitation reactions can be carried out with less complex manifolds. The absence of an air stream in FIA would offer a reduced number of flow-channels and more efficient filtration in its manifold than SFA. Thus, Martinez-Jimenez and coworkers\textsuperscript{19,20} reported two manifold configurations that incorporated filter units originally designed for solvent cleaning in HPLC (Scientific System 0.5-105 column with removable stainless steel membrane, 0.5 \textmu m pore-size, 3 cm\textsuperscript{2} filter area and 580 \textmu l volume) for continuous precipitation in FI-flame AAS. The design of the manifolds is shown in Fig. 4.2. Fixed volumes of samples (or reagent, for reversed FIA) were injected into the stream of the cation reagent (or sample, for reversed FIA) and the precipitates were retained by the on-line filter whilst the effluents passed on to the AAS. The unretained cation was measured by the AAS. The filter unit was washed at intervals in an ultrasonic bath to prevent clogging but this was not necessary when the manifold was designed for precipitation followed with on-line dissolution. The authors reported that crystalline precipitates caused more clogging of the conduits than curdy or gelatinous precipitates. The applications of the two manifold configurations in the assay of organic and inorganic species in water, food and pharmaceutical samples have been outlined in section 1.7.
On-line precipitation and filtration is such a recent development in FIA that the number of publications to date (late 1989) is less than twenty. Flame atomic absorption spectrometers are the on-line detectors reported in these publications. There are yet no reports of the use of other detectors such as solution spectrophotometers and electrochemical detectors. In addition, a method development that would deviate from the mere imitation of the conventional manual precipitation-dissolution procedure needs to be established. Therefore, a study of the manifold design and the optimisation procedure for carrying out on-line precipitations is presented in this chapter. Precipitation-dissolution reactions involving basic calcium oxalate were used and tested for the removal of interferents in the flame atomic absorption spectrometry of calcium. Filtration devices, assembled in-house as a packed bed of inert materials with and without polymer...
membrane filters, as well as cheap disposable syringe filters, which are of routine use in chemistry, were studied. The chapter concludes with the application of the developed procedure to determine calcium in two different samples of cement.

4.2. APPARATUS AND REAGENTS

The manifolds used in the experiments were constructed from PTFE tubing of internal diameter 0.58 mm. The peristaltic pump was a Gilson Minipuls-2 fitted with PVC tubing of 0.4 mm internal diameter for the water-carrier and the reagent streams. Pump tubing of 2.05 mm internal diameter was used for the acid stream where stream elution was applied for precipitate dissolution. The arms of a four-way rotary valve (low pressure Rheodyne 5041) were cut for the injections of volumes less than 50 µl. A two-way valve (Anachem) was used to switch streams except where indicated in which case a three-way rotary valve (Rheodyne 5301) was used for multiple stream-switchings. The Y- and T- connectors were made, in-house, from transparent glass to permit visual observation of the reagent- and air-mixing processes. The merging point of the Y- connector, where indicated, was blown to approximately 2 ml and packed with glass helixes (diameter of about 3 mm) to study further the mixing process in the manifold. The minicolumn (a PVC pump tube packed with glass beads), disposable membrane filters (Gelman syringe filters, of 0.45 µm pore-sizes and filter diameters 3, 13 and 25 mm) and a stainless steel disc filter (2 µm pore-size, 6 mm filter diameter and 2 mm thickness) were used to study the efficiency of the collection of precipitates. The precoils and the pulse dampers have been described in section 2.2.

The drain tube of the atomic absorption spectrometer, Baird-Atomic, Model A3400, was adapted to drain by suction as it was used to measure nebulisation efficiencies in Chapter 2 (see Fig. 2.1.(iii)). The spectrometer was connected to a Philips AR55 chart recorder for absorbance measurements.

Calcium solutions were prepared by diluting stock 1000 mg l⁻¹ solutions (BDH spectrosoL grade). Aluminium chloride (minimum assay 97%) was used as interferent. The standard solutions of calcium, which contain 10 mg l⁻¹ Ca with aluminium in the range 0 - 200 mg l⁻¹, were used as test samples. The ammonia-ammonium ion buffer/reagent solutions were prepared from ammonia solution (for food stuff analysis), ammonium chloride and ammonium oxalate monohydrate (≥ 99% purity with maximum calcium impurity of 0.001%). These
4.3. PRELIMINARY EXPERIMENTS: Effect of selective precipitants on calcium/aluminium interference using flow injection analysis

The depressive effect of aluminium on the absorbance of calcium in FAAS has been studied in section 3.5. The results of the experiments showed that the absorbance of 10 mg l\(^{-1}\) Ca decreased continuously as the concentration of aluminium increased. The effect persisted in acetylene-air flame when the instrument parameters (fuel composition, burner height, and the capillary tip position in its venturi nozzle) were carefully adjusted without the addition of releasing agents. The effect also persisted on the application of FI-techniques without any chemical reaction. Therefore a method that would selectively separated calcium from aluminium had to be devised. To achieve this, the analytical procedures for the selective precipitation of aluminium and calcium with ammonia or ammonium salts\(^{29-31}\) were adapted to FIA.

4.3.1. Effect of ammonia

Basis of the method_ The precipitation reactions for calcium and aluminium ions with hydroxide ions, in aqueous solution, are represented by equations 4.1 and 4.2.

\[
\begin{align*}
\text{Al}^{3+} + 3 \text{OH}^- & \rightarrow \text{Al(OH)}_3 \quad \text{(s)} \quad \text{4.1} \\
\text{Ca}^{2+} + 2 \text{OH}^- & \rightleftharpoons \text{Ca(OH)}_2 \quad \text{(s)} \quad \text{4.2} \\
\text{NH}_3 (\infty) + \text{H}_2\text{O} & \xrightarrow{k_b} \text{NH}_4^+ + \text{OH}^- \quad \text{4.3}
\end{align*}
\]

The quantitative precipitation of aluminium occurs from pH 5 upwards whilst that of calcium occurs from pH 10 upwards. Ammonia, being a weak base (see Equation 4.3; \(pK_b = 1\) M \text{NH}_3, at 25°C equals 4.74), is expected selectively to precipitate aluminium in a solution that contains calcium.

The reactants for the precipitation are brought into contact using the dispersions...
afforded in a single line manifold. The use of low pumping flow rates and long reaction coils are expected to increase the contact time for the reactants and favour the complete precipitation of aluminium hydroxide.

The initial concentrations of the ammonia solutions were prepared to be about identical and in excess of the stoichiometric equivalent of the top concentration of the aluminium interferent to afford a complete precipitation.

Procedure and results. The spectrometer was operated at the conditions for the determination of calcium at maximum sensitivity as shown in Table 4.2. The nebuliser liquid uptake, for conventional aspiration with the set conditions, was 8.2 ml min\(^{-1}\).

| Table 4.2. Optimum conditions for calcium on Baird-Atomic, Model A3400, spectrometer. |
|-----------------------------------------------|-----------------|
| wavelength, nm                                | 422.7           |
| slit width, nm                                | 0.5             |
| lamp current, mA                              | 2.2             |
| supporting gas/ flow rate, \(1\) min\(^{-1}\) | air/7.5         |
| fuel gas/ flow rate, \(1\) min\(^{-1}\)       | acetylene/3.2   |
| burner height, cm                             | 2.5             |
| read out                                      | direct          |
| scale expansion                               | 1               |
| curve correction                              | linear          |
| damping                                       | off             |
| impact bead                                   | optimum*        |
| capillary tip adjustment                      | about 0.5 mm into its housing. |

* manufacturer's reference, bead was close to the nebuliser venturi nozzle.

The single line manifold, shown in Fig. 4.3, was used. The water carrier stream was pumped at 1.0 ml min\(^{-1}\) and 38 µl injections of each test solution (10 mg l\(^{-1}\) Ca with aluminium in the concentration range of 0 - 100 mg l\(^{-1}\)) were made in triplicates. The absorbances were recorded on chart at a speed of 60 s cm\(^{-1}\). The
Fig. 4.3. Single line manifold for the continuous precipitation and filtration of aluminium hydroxide from solutions that contain calcium.

Fig. 4.4. Effect of selective and continuous precipitation of aluminium hydroxide on the absorbance of 10 mg l⁻¹ Ca in a single line manifold. 38 μl injections for: (●), water; (○), 0.005 M; (□) 0.01 M; and (∆), 0.02 M ammonia; carrier streams at 1.0 ml min⁻¹.
plot of the averaged peak heights against the concentration of aluminium produced a calcium/aluminium interference curve of trend similar to that previously observed in section 3.5. The procedure was repeated for 0.005 M NH₃, 0.01 M NH₃ and 0.02 M NH₃ each used as carrier stream. The plot of the averaged peak heights against the concentration of aluminium produced different calcium/aluminium interference curves as shown in Fig. 4.4.

Conclusions and comments_ The ammonia reagent showed the potential for the complete removal of calcium/aluminium interference when its concentration (0.02 M NH₃) was five-fold in excess over the highest concentration of aluminium (100 mg l⁻¹ is about 0.004 M). The absorbance of calcium with or without the aluminium interferent was, however, reduced in this carrier stream compared with the absorbance of simple calcium in water carrier stream. An injection of 38 µl of 1 M HCl into the 0.02 M NH₃ carrier stream, after the sample had been injected, produced a sharp peak of high absorbance for calcium. This showed that the selective precipitation of aluminium hydroxide by the injection of fixed volumes of test solutions into the carrier stream of ammonia, in a single line manifold, caused the simultaneous precipitation of calcium. The effect caused the recorded absorbance profiles of calcium in an ammonia carrier to be significantly narrower (that is, of reduced peak width) than those recorded for a water carrier stream.

4.3.2. Effect of ammonia-ammonium chloride

The single line manifold of Fig. 4.3 was used. The procedure described in section 4.3.1 was carried out for the ammonia-ammonium chloride solutions, shown in Table 4.3, which were used in turn as the carrier stream. The injection of 38 µl of 1 M HCl into the 0.020 M NH₃ with 0.20 M NH₄Cl carrier stream, after the sample had been injected, gave no absorbance for calcium. Therefore the use of ammonia-ammonium chloride solutions as carriers prevented the precipitation of calcium but it was only partly successful in removing the calcium/aluminium interference. The results are shown in Fig. 4.5.
Table 4.3. Composition of solutions of ammonia with ammonium chloride used for on-line selective precipitation of aluminium

<table>
<thead>
<tr>
<th>solution</th>
<th>ammonia</th>
<th>ammonium chloride</th>
<th>pH *</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.020 M</td>
<td>0.20 M</td>
<td>8.1</td>
</tr>
<tr>
<td>2</td>
<td>0.008 M</td>
<td>0.20 M</td>
<td>7.8</td>
</tr>
<tr>
<td>3</td>
<td>0.002 M</td>
<td>0.20 M</td>
<td>7.1</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>0.02 M</td>
<td>4.3</td>
</tr>
</tbody>
</table>

* measured with Aqua Scientific, alpha 600, pH-meter.

Fig. 4.5. Effect of selective and continuous precipitation of aluminium hydroxide on the absorbance of 10 mg l⁻¹ Ca in a single line manifold. Sample volumes of 38 µl injected into: (●), water; (○), 0.002 M NH₃ with 0.20 M NH₄Cl; (□), 0.008 M NH₃ with 0.20 M NH₄Cl; (▲), 0.02 M NH₃ with 0.20 M NH₄Cl; and (●), 0.02 M NH₄Cl; as carrier streams at 1.0 ml min⁻¹.
All the solutions when used as carriers produced higher absorbance for 10 mg l\(^{-1}\) calcium than for a water carrier and the result for a 0.002 M ammonia with 0.20 M ammonium chloride (pH 7.1) carrier showed the largest reduction in the depression caused by aluminium.

There was a limit to the concentration of ammonium chloride that could be used to prevent the precipitation of calcium because the carrier streams which contained more than 0.20 M NH\(_4\)Cl caused an absorbance base line shift at the pumping flow rate of 1.0 ml min\(^{-1}\). In addition, the flame was luminous and the resulting light scatter caused erratic peaks hence high concentrations of ammonium chloride, greater than 0.20 M, were not used.

Additional experiments were designed to improve further the selective precipitation of aluminium hydroxide. These experiments and the results are summarised below:

(a), the application of an increased pumping flow rate of up to 3.6 ml min\(^{-1}\) with stopped-flow FIA (up to 160 s stopped-flow during which interval, the air compensation inlet was dipped into a water reservoir so as to minimise the carrier stream being drawn by nebuliser suction), had no significant effect on the calcium/aluminium interference curve;

(b), the reagent reservoir was heated to 57 °C in a water bath and pumped as a hot carrier stream. The increased reaction temperature caused about 20\% increment in the absorbance of 10 mg l\(^{-1}\) Ca. The calcium/aluminium interference, however, remained unimproved; and

(c), a membrane filter of smaller pore-size (0.2 \(\mu\)m) was incorporated into the manifold for the continuous filtration of aluminium hydroxide. The size of the filter pore had no significant effect on the absorbance trend. Moreover, it was observed that the decreased depression of the absorbance of calcium by aluminium in the carrier streams of buffers or ammonium chloride solution occurred with or without the on-line membrane filter (see Fig. 4.6).

The results showed that the single line manifold (in Fig. 4.3) could not adequately effect the complete separation of aluminium from an injected sample of calcium. The 0.002 M NH\(_3\) with 0.2 M NH\(_4\)Cl was the carrier stream in all the experiments.
Fig. 4.6. Effect of selective and continuous precipitation of aluminium hydroxide on the absorbance of 10 mg l$^{-1}$ calcium in a single line manifold. Sample volumes of 38 μl were injected into: (.), water carrier; and (o), 0.002 M ammonia with 0.2 M ammonium chloride; carrier streams pumped at 3.6 ml min$^{-1}$.

(A), manifold was with on-line filter; and (B), manifold was without on-line filter.
4.3.3. Effect of mixed solvents

The gelatinous nature of the precipitate of aluminium hydroxide could cause its precipitation, at low concentrations, to form a colloidal solution and hence the precipitates would not be retained by the filter. For this reason, a mixed solvent (water with ethanol) was chosen to condition the precipitate so that the precipitate might coagulate.

Fig. 4.7. Two-line manifold used for the separation of aluminium from calcium by continuous precipitation and filtration of aluminium hydroxide in a mixed solvent matrix.

The two lines manifold shown in Fig. 4.7 was used to study the effect of ethanol on the selective precipitation of aluminium hydroxide. The reagent, 0.002 M ammonia with 0.20 M ammonium chloride solution, was pumped at 0.76 ml min\(^{-1}\) and 128 \(\mu l\) injections of each test solution (10 mg l\(^{-1}\) Ca with aluminium in the range of 0 - 100 mg l\(^{-1}\)) were made in triplicates. The reagent carrier was merged with the ethanol stream which was pumped at 0.32 ml min\(^{-1}\) prior to the on-line filtration. The absorbances were recorded on chart at 60 s cm\(^{-1}\). The experiment was repeated.
The plots of the averaged peak heights against the concentration of aluminium are shown in Fig. 4.8.

![Graph showing the effect of selective and continuous precipitation of aluminium hydroxide on the absorbance of 10 mg l\(^{-1}\) calcium. Sample volumes of 38 µl were injected into an aqueous carrier stream which was merged with ethanol of flow rate, 0.32 ml min\(^{-1}\): (○), water; (○), 0.002 M NH\(_3\) with 0.2 M NH\(_4\)Cl; (Δ), 0.02 M NH\(_3\) with 0.2 M NH\(_4\)Cl; and (□), 0.2 M NH\(_3\) with 0.2 M NH\(_4\)Cl; as carriers at 0.76 ml min\(^{-1}\).]

The absorbance of 10 mg l\(^{-1}\) Ca decreased as the concentration of aluminium increased. This trend was similar to those observed when reagents of similar composition were used as carriers in a single line manifold without the ethanol solvent. Therefore ethanol had no significant effect on the precipitation (coagulation) of aluminium hydroxide.

The experiment was repeated in which high pumping flow rates (up to 2.1 ml min\(^{-1}\) for the reagent stream and 0.6 ml min\(^{-1}\) for the ethanol stream) were used. The increased pumping flow rates, however, had no significant effect on the trend of absorbance of calcium/aluminium interference.
4.3.4. Effect of ammonium oxalate

The reagents used so far, failed to separate completely calcium from aluminium. Therefore, the approach used for the separation of calcium from aluminium was changed from the precipitation of aluminium to the precipitation of calcium. To this effect, an ammonium oxalate solution was chosen as the reagent and as carrier stream for the precipitation which was carried out first in a single line manifold and then in a two-line manifold.

Application of the single line manifold

The single line manifold (see Fig. 4.3) and the procedure were both similar to section 4.3.1 except that the solutions shown in Table 4.4 were each used as carrier streams in turn. The injections of the test solutions (10 mg l\(^{-1}\) Ca with aluminium in the range, 0 - 100 mg l\(^{-1}\)) into the manifold, however, produced no obvious precipitation of calcium. In addition, there was no precipitation when the following adjustments were carried out in the single line manifold:

(a), the length of the manifold reaction coil, \(R_c\), was increased to 1.5 m; (b), the reaction coil was replaced with a string of beads 25 cm long; and (c), application of up to 6 minutes stopped-flow.

<table>
<thead>
<tr>
<th>solution</th>
<th>ammonia</th>
<th>ammonium oxalate</th>
<th>pH *</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>0.001 M</td>
<td>5.9</td>
</tr>
<tr>
<td>2</td>
<td>0.002 M</td>
<td>0.001 M</td>
<td>8.8</td>
</tr>
<tr>
<td>3</td>
<td>0.02 M</td>
<td>0.001 M</td>
<td>9.6</td>
</tr>
<tr>
<td>4</td>
<td>0.10 M</td>
<td>0.001 M</td>
<td>10.1</td>
</tr>
</tbody>
</table>

* measured with Aqua Scientific, alpha 600, pH-meter.

Application of a two-line manifold

The two lines manifold shown in Fig. 4.9 was devised. A packed bed reactor was incorporated into the manifold to increase radial mixing. The use of the packed bed reactor also avoided the problem of back pressures which was observed when a reaction coil (tube of 2.5 cm length, i.d. 0.8 mm and coil diameter 2 cm) or a string of glass beads (i.d. 0.05 mm, packed into 50 cm tube length and tube i.d. 0.8 mm) was incorporated into the
The ammonium oxalate reagent was used as the carrier stream and it was merged with water, hydrochloric acid, ammonium chloride and ammonia solutions in turn. The ammonium oxalate with ammonia solutions were the reagent combination that formed precipitates with calcium.

**Procedure and results** -- The 0.001 M (COONH₄)₂ carrier stream and the 0.10 M NH₃ stream were each pumped at 1.9 ml min⁻¹. The packed beads were lagged at about 50 °C and 70 μl of a test solution were injected, in triplicate, into the oxalate carrier stream. No absorbance peak was observed. A 38 μl injection of 50% (v/v) HCl into the ammonia stream, however, produced a sharp peak which was recorded on chart at 60 s cm⁻¹. The procedure was carried out for each test solution and the entire procedure was repeated for water streams instead of the reagent streams. The
injection of 70 μl of the test solutions into the water carrier stream produced peaks whilst the injection of 38 μl of 50% HCl showed no peaks. The plot of the results are shown in Fig 4.10.

![Graph showing absorbance against concentration of aluminium, mg l⁻¹.](image)

**Fig. 4.10.** Effect of selective precipitation of basic calcium oxalate on the absorbance of 10 mg l⁻¹ calcium in a two-line merging-streams manifold. (Δ), carrier stream of 0.001 M (COONH₄)₂ merged with 0.10 M NH₃ stream, each pumped at 1.9 ml min⁻¹. Sample injection was 70 μl- triplicates, followed with one 38 μl- injection of 50% HCl to dissolve the precipitates. (●), normal calcium/aluminium interference curve, 70 μl injections into water stream.)

Conclusions and comments -- The ammonia- ammonium oxalate system has the ability to remove the depression of calcium absorbance due to aluminium interference. Other interferents which neither form precipitates nor elute at the same time with calcium in the reaction system would also be removed. The reagent system has the ability to preconcentrate calcium from a large volume of solution. The low pumping flow rate, of about 1.9 ml min⁻¹ had to be used in the experiments to avoid the back pressures which caused the manifold to leak at its connections. This low flow rate, however, would reduce sample throughput.

4.3.5. Discussion

The preliminary experiments in this report show the feasibility of incorporating a continuous filtration device into an FIA manifold. A 0.001 M ammonium oxalate
reagent selectively precipitated 10 mg l⁻¹ Ca from a solution of up to 100 mg l⁻¹ aluminium in a two-line manifold. The manifold permitted a 0.10 M ammonia stream to be added equally to all segments of the dispersed sample zone in the ammonium oxalate carrier (see Fig. 4.11(II)). This resulted in the precipitation of

![Diagram](image_url)

Fig. 4.11. Hypothetical flow curves for the concentration profiles of reaction components in a manifold for precipitation with filtration and precipitate dissolution.

(I), single line manifold; and (II), two-line manifold.

$C^0$, initial concentration; $C_{\text{max}}$, concentration at peak maximum; F, filter; I, sample injection; R, reagent; $R_c$, reaction coil; S, sample; P, product; $P_E$, peak of dissolved product; t, time; and D, detector.
calcium oxalate which was retained by the filter.

The 0.001 M ammonium oxalate with 0.10 M ammonia, used as a carrier, could not precipitate calcium in a single line manifold. This could be due to the reduced extent of mixing afforded by the manifold as well as the slow kinetics of the calcium/oxalate reaction. On the other hand, a 0.020 M ammonia solution, used as a carrier stream, partially precipitated calcium. In this case, the reaction kinetics was not a constraint. It could be that the injected sample zone and the reagent carrier, when dispersed into each other, could only aid the precipitation of calcium, more at the wings of the dispersed sample zone than at the centre (see Fig. 4.11(I)). These wings are the regions with ever increasing reagent concentration. The central segment of the sample zone, has no or low reagent concentration to precipitate calcium. Hence, this segment passed through the filter and gave a narrow absorbance profile for calcium at the detector. This would explain the narrow absorbance peaks observed for calcium in ammonia streams in section 4.3.1. The partial precipitation of calcium was, however, reproducible but it offered no useful trend in the removal of aluminium because the reaction was not buffered. Similar explanations can be adduced for the precipitation of aluminium in a single line manifold. Thus, the axial dispersions of the sample and reagent in a single line conduit could not maintain the required reactant proportions over the entire sample zone to enable the complete precipitation of either aluminium hydroxide or calcium oxalate. Hence the calcium/aluminium interference was partially reduced in sections 4.3.2 and 4.3.3.

The precipitation of aluminium hydroxide would have been better carried out in a two-line manifold but this approach was not pursued in this report because the sample bolus would be so much dispersed that peak height quantification would be of reduced sensitivity. In addition, the thermodynamics of the reaction would always leave traces of aluminium in the sample bolus which would depress the absorbance of calcium. Therefore, the alternative approach in which calcium was precipitated and washed free from aluminium (as reported in section 4.3.4) has the merits of a complete removal of the aluminium interference as well as a potential for peak height sensitivity enhancement.

4.3.6. Conclusions

The chemical separation of calcium from aluminium in FIA, using the selective precipitation of calcium followed by filtration and subsequent dissolution of the
precipitates completely removed the aluminium depression.

The precipitation-dissolution procedure, as adapted to a flow injection technique, minimised the clogging of the filter unit. The procedure has the potential advantages of FIA such as using a limited sample volume in a contamination free environment as well as enhancing sensitivity over conventional FAAS through the preconcentration of calcium from a large volume of test solution.

4.4. OPTIMISATION OF THE DETERMINATION OF CALCIUM USING CALCIUM OXALATE PRECIPITATION IN FIA

4.4.1. Basis of the method

The precipitation reaction between calcium and oxalate ions in ammonia-ammonium oxalate buffer is represented in equation 4.4.

\[
\text{NH}_3 (aq) + (\text{COONH}_4)_2 (aq) + 2 \text{Ca}^{2+} (aq) + 2 \text{H}_2\text{O} \rightleftharpoons \{ \text{Ca(OH)}_2, \text{Ca(OCO)}_2 \} (s) + 4 \text{NH}_4^+ \tag{4.4}
\]

The formation of the basic calcium oxalate precipitate may not attain a thermodynamic steady state in the flowing stream of the reagents but it has to be reproducible. The dissolution of the precipitate as represented in equation 4.5 has to be quantitative and reasonably instantaneous so as to avoid 'carry overs' and tailing peak-profile.

\[
\{ \text{Ca(OH)}_2, \text{Ca(OCO)}_2 \} (s) + 4 \text{H}^+ \rightarrow 2 \text{Ca}^{2+} + (\text{COOH})_2 + 6 \text{H}_2\text{O} \tag{4.5}
\]

The two-line manifold used in section 4.3.4 (see Fig.4.9) was developed further. The relative initial operating concentrations and the pumping flow rates of the sample to the reagent were predicted from the following assumptions: 32

(a), the dilution factor (dispersion, \(D_o\)) of the injected sample would be greater than 1, a value which is dependent almost entirely on the flow rates of the carrier and reagent streams;

(b), the addition of the reagent to all the segments of the sample zone would be uniform and constant at the confluence point; and

(c), thorough mixing occurred at the confluence point such that other subsequent dispersions are insignificant to the precipitation process.
Let

\[ C_s^0 \] be the injected sample concentration;
\[ C_R^0 \] be the concentration of the reagent;
\[ C_s^{\text{max}} \] be the concentration of sample at peak maximum;
\[ C_R \] be the concentration of the reagent in the sample;
\[ u_s \] be the pumping flow rate of the sample;
\[ u_R \] be the pumping flow rate of the reagent;
\[ D_s \] be the dilution factor of the sample; and
\[ D_R \] be the dilution factor of the reagent.

Then,

\[ C_R = C_R^0 / D_R = C_R^0 [u_R / (u_s + u_R)] \]  ............................................. \( 4.6 \)

and

\[ C_s^{\text{max}} = C_s^0 / D_s = C_s^0 [u_s / (u_s + u_R)] \]  ............................................. \( 4.7 \)

from equation 4.4,

\[ 1 \text{ mole NH}_3 = 1 \text{ mole oxalate ion} = 2 \text{ mole Ca}^{++} \]

Therefore, to obtain an excess of reagent over determinand following mixing,

\[ C_R^0 [u_R / (u_s + u_R)] \geq \frac{1}{2} \cdot C_s^0 [u_s / (u_s + u_R)] \]  ............................................. \( 4.8 \)

In which case,

\[ \text{if} \ u_s = u_R, \ \text{then} \ C_R^0 \geq \frac{1}{2} \cdot C_s^0 \]

The flow rate condition in Equation 4.8 was used as a guide such that identical pump tubes were chosen for the reagent and the sample carrier streams. The initial concentrations (mol. dm\(^{-3}\)) of the ammonia with the ammonium oxalate reagents were however prepared to be in excess (about a factor of five) of the stoichiometric equivalent concentrations of the calcium with or without the aluminium interferent. The excess reagent was expected to make the reaction proceed in the presence of the experimental constraints such as the difficulty of matching the flow rates of the streams and the uncertainty of the reagent and the sample to mix thoroughly.
4.4.2. Optimisation of Reaction Conditions

The spectrometer was set for the determination of calcium at maximum sensitivity and the conditions shown in Table 4.2 (see section 4.3.1) were used. The conventional liquid uptake of the nebuliser with the optimum conditions was 8.0 ml min\(^{-1}\). The two line manifold used in section 4.3.4 was adjusted as shown in Fig. 4.12.

**Fig. 4.12.** Two-line manifold for the continuous precipitation, filtration and dissolution with fixed volume elution for calcium. C, water carrier; R, ammonia-ammonium oxalate reagent; P\(_c\), precoil; P\(_s\), pulse damper; I, injection point; m, minicolumn of glass beads; g, guard column (PVC tube, 3 cm long and 1.6 mm i.d.); v, 2-way stream switching valve; and a, air compensation inlet. (Y-connector and T-piece were made from glass tubing, 0.6 mm i.d.).
The minicolumn of glass beads was used to retain the precipitates without the cellulose acetate filter. The reagents were made up together in one solution. The solution was used as a reagent stream to satisfy the addition of reagents in equal amounts to all segments of the dispersed sample zone. The slow reaction kinetics of the calcium/oxalate reaction were taken into consideration and low pumping flow rates were therefore chosen in preference to a long reactor to increase the reaction contact time.

Reaction conditions such as temperature and the concentration of the buffer as well as the manifold parameters were varied individually while others were kept constant for the optimisation procedure.

4.4.2. (i) Effect of temperature; and (ii) Effect of varying ammonia concentration.

Procedure and results -- The manifold shown in Fig. 4.12 was used. The composition of the buffer reagent was 0.10 M ammonia with 200 mg l⁻¹ (about 0.014 M) ammonium oxalate monohydrate (AOM). Water was pumped at 0.68 ml min⁻¹ and merged with the buffer flowing at 0.76 ml min⁻¹. The minicolumn and the guard column were placed in a boiling tube fitted into a lagged polythene wash-bottle. The bottle was adapted such that water at a specific constant temperature was circulated in and out of it from an external water bath with a pump. A solution of 5 % HCl was used as the eluting solvent and 39 μl volumes were repeatedly injected into the water stream to wash the reactor to an acceptable blank absorbance of about 0.010. Then 39 μl volumes of the test solutions were injected coupled with an identical injection of 5% HCl to elute the precipitate after a two-minute delay for each injection. The precipitation-dissolution injection cycle was replicated three times for each test solution. The absorbances were recorded on chart at 120 s cm⁻¹. The procedure was carried out at different temperatures and repeated for water merged with the different concentrations of the reagents shown in Table 4.5. The interference curve for 10 mg l⁻¹ calcium in the test solutions was obtained at room temperature (22 °C) by the injections of the test solutions into the water carrier stream. The carrier stream was merged with water, without the reagent, in the manifold. The plots of these results are presented in Fig. 4.13 and Fig. 4.14.

Figure 4.13 shows that the pH 10 reagent precipitated calcium at room (22 °C) and high temperatures with approximately similar removal of the interference caused by
Table 4.5. Reagent composition and the temperature variations in the optimisation procedure of section 4.4.2.

<table>
<thead>
<tr>
<th>reagent stream</th>
<th>pH</th>
<th>temperatures for repeat runs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 0.10 M NH₃ with 200 mg l⁻¹ AOM</td>
<td>10.2</td>
<td>50 °C, 60 °C and 70 °C</td>
</tr>
<tr>
<td>2. 0.05 M NH₃ with 200 mg l⁻¹ AOM</td>
<td>10.2</td>
<td>22 °C and 65 °C</td>
</tr>
<tr>
<td>3. 0.01 M NH₃ with 200 mg l⁻¹ AOM</td>
<td>9.0</td>
<td>22 °C, 50 °C and 70 °C</td>
</tr>
<tr>
<td>4. 0.001 M NH₃ with 200 mg l⁻¹ AOM</td>
<td>8.3</td>
<td>22 °C and 50 °C</td>
</tr>
</tbody>
</table>

* alpha 600 pH-meter (Aqua Scientific) was used to measure the pH of the solutions.

Fig. 4.13. Selective precipitation of 10 mg l⁻¹ calcium followed by fixed volume dissolution with HCl(α) in manifold 4.12. Effect of temperature and 0.10 M ammonia with 200 mg l⁻¹ ammonium oxalate (AOM) reagent (pH 10): (α), 50 °C; (●), 60 °C; (○), 70 °C. (●), interference curve for calcium, in water streams without reagent at 22 °C.)
Fig. 4.14. Selective precipitation of 10 mg l⁻¹ calcium followed by fixed volume dissolution with HCl(aq) in manifold 4.12. Effect of the concentration of ammonia in 200 mg l⁻¹ ammonium oxalate (AOM) reagent: (θ), 0.001 M ammonia (pH 8); (●) 0.01 M ammonia (pH 9); (●) 0.05 M ammonia (pH 10) and the reaction temperature was 22 °C. (θ), interference curve for calcium, in water streams without reagent at 22 °C.}

aluminium. The efficiency and the selectivity of calcium precipitation improved with increased concentration of the ammonia (that is, with increased pH of the reagent). Thus, the absorbance of 10 mg l⁻¹ calcium with ≥20 mg l⁻¹ aluminium was constant in 0.05 M ammonia (see Fig. 4.14).

Conclusions and comments -- The optimum ammonia concentration was 0.05 M and the precipitation reaction could occur reproducibly at room temperature as well as at high temperatures. It was, however, important that the reagents (especially the buffer) were protected from calcium contamination which could cause shifts in the absorbance base line as well as poor precision of absorbances due to the possible experimental fluctuations in the duration of the injection cycle. Hence the reagents were prepared daily and the reagents as well as the water carrier were kept in covered polythene bottles throughout the experiments. Air bubbles, when conspicuous, were flushed out of the streams to improve the precision of peak height absorbance.
4.4.2. (iii) Effect of varying oxalate concentration

Procedure and results -- The manifold shown in Fig. 4.12 was used and the operation sequences were identical to those used in section 4.4.2.(i). The procedure was carried out at room temperature for seven reagent streams. The concentration of the ammonium oxalate monohydrate in 0.05 M ammonia was varied in the range of 0 to 200 mg l\(^{-1}\). The results are shown in Fig. 4.15.

Fig. 4.15. Selective precipitation of 10 mg l\(^{-1}\) calcium followed by fixed volume elution with HCl (\(\beta\)) in manifold 4.12.
Effect of the concentration of ammonium oxalate (AOM) with 0.05 M ammonia reagent: (\(\alpha\)), 5 mg l\(^{-1}\) (pH 10.8); (\(\beta\)), 10 mg l\(^{-1}\) (pH 10.6); (\(\gamma\)), 50 mg l\(^{-1}\) (pH 10.5); (\(\delta\)), 200 mg l\(^{-1}\) (pH 10.3).
(\(\Theta\)), interference curve for calcium, in water streams without reagent at 22°C.)

The increased concentration of the oxalate caused the pH of 0.05 M ammonia (pH 10.6) to decrease in fractions such that the reagent stream which had 50 mg l\(^{-1}\) AOM showed a constant absorbance for 10 mg l\(^{-1}\) calcium with 30 mg l\(^{-1}\) to 200 mg l\(^{-1}\) aluminium (the highest concentration of the test solution). The reagents with concentrations lower than 50 mg l\(^{-1}\) oxalate offered reduced selectivity in the removal of aluminium interference whilst the reagent with concentration higher than
50 mg l\(^{-1}\) oxalate offered a similar selectivity in the removal of aluminium interference but with reduced sensitivity.

Conclusions and comments -- The concentration of ammonium oxalate (AOM) that offered maximum sensitivity for 10 mg l\(^{-1}\) Ca was 50 mg l\(^{-1}\). A concentration greater than 50 mg l\(^{-1}\) AOM, however, appeared to afford better precision. It was observed that the injection of a large volume (about 100 μl) of simple 10 mg l\(^{-1}\) calcium into the manifold gave absorbance signals for the precipitation effluents. The absorbance profile of the effluents broadened and tailing was observed when 0.05 M ammonia with 200 mg l\(^{-1}\) AOM was used. This showed that the precipitation of calcium was incomplete in the reagent with 200 mg l\(^{-1}\) AOM and the precipitates were being stripped by the reagent stream. The reagent with 200 mg l\(^{-1}\) AOM, therefore, offered precise absorbance in the experiment because the durations of the 'wash' in the precipitation-dissolution cycles were kept constant. The reagent, 0.05 M ammonia with 50 mg l\(^{-1}\) ammonium oxalate, showed no such tailing and hence was chosen as the optimum reagent composition for further experiments.

4.4.2. (iv) Effect of the acidity of sample matrix

The effect of the acid content of a sample of calcium on its precipitation with the optimum reagent composition (0.05 M ammonia with 50 mg l\(^{-1}\) ammonium oxalate) was studied.

Procedure and results -- The manifold in Fig. 4.12 was used. Seven test solutions, each containing 10 mg l\(^{-1}\) Ca with hydrochloric acid in the range of 0 to 20 percent (v/v), were used in this experiment. Water carrier stream was merged with the buffer (0.05 M ammonia with 50 mg l\(^{-1}\) AOM) at a total pumping rate of 1.37 ml min\(^{-1}\). Three replicate precipitation-dissolution cycles were carried out for each test solution. The injection volume was 39 μl for the solutions and for the 5% HCl which was used to dissolve the precipitates. The results, shown in Fig. 4.16, were compared with the results from identical volume injections into water streams without reagent and with the conventional aspiration of the test solutions at the nebuliser liquid uptake rate of 8 ml min\(^{-1}\).

Conclusions and comments -- The precipitation of calcium with the ammonia/oxalate buffer was optimum for the sample matrix which was neutral or with the acid concentration less than the equivalent concentration of the ammonia component of the buffer, below 0.5% HCl (0.05 M HCl). The absorbances of the
Fig. 4.16. Effect of acidity of sample matrix on the precipitation of 10 mg l\(^{-1}\) calcium in manifold 4.12.

Reagent stream was 0.05 M NH\(_3\) with 50 mg l\(^{-1}\) AOM. (I), 39 \(\mu\)l injections into water stream at 0.7 ml min\(^{-1}\):

- (I), 5% HCl elution of the precipitates; (o), precipitation effluent.
- (II), conventional aspiration at 8 ml min\(^{-1}\), (●).
- (●), curve for calcium, in water streams without reagent at 22\(^{\circ}\)C.

Precipitation effluents showed that the acid in the sample zone neutralised the ammonia to offer similar peak absorbances as the injections of samples, with low acid content, into water stream. The absorbance profiles of the precipitation effluents, however, were narrower than for water stream because the reagent and the water carrier stream were observed as segmenting each other instead of a perfect mix. Therefore, the segments from the peak maximum of the sample zone having incomplete or no precipitation reaction showed the narrow absorbance.
profiles. Stream segmentation was visually observed to occur as from the confluence T-piece when coloured water was pumped to merge with a water stream instead of the reagent stream.

The depressive effect of hydrochloric acid on the absorbance of calcium was completely removed not by the physical operational parameters of the manifold alone, but with the chemical reaction of the buffer. This is shown by the absorbance curves of both the precipitation effluent and the water stream without reagent in Fig. 4.16.(I).

4.4.3. Optimisation of flow injection parameters:

(i) Effect of pumping flow rate

Procedure and results -- The manifold shown in Fig. 4.12 was used and the water carrier stream was merged with the buffer stream each pumped at 0.22 ml min⁻¹. The composition of the buffer was 0.05 M ammonia with 50 mg l⁻¹ AOM, which were the optimum conditions from the results of experiments 4.4.2.(ii) and 4.4.2.(iii). Sample volumes of 39 μl were injected into the water stream for the precipitation-dissolution cycles of each test solution (10 mg l⁻¹ Ca with different concentrations of aluminium from 0 to 200 mg l⁻¹). The injection cycle was replicated twice for each test solution and the absorbances were recorded on chart at 120 s cm⁻¹. The pumping flow rate of the streams was gradually increased by the adjustment of the pump rotation speed control and the entire procedure was repeated at the different settings that offered pumping flow rates of up to 1.33 ml min⁻¹ for each stream. The experiment was carried out at room temperature and the results are shown in Fig. 4.17. The observed characteristics of the absorbance profiles in the duration of this experiment are summarised in Table 4.6.

Conclusions and comments -- The absorbance of calcium increased to a maximum, and then decreased, as the pumping flow rates of both the reagent and the solvent streams increased. The flow rate that afforded maximum sensitivity for calcium was 1.37 ml min⁻¹. A slightly lower flow rate than the optimum could have caused a decrease in the sensitivity of calcium: (a), because more time than the five minutes used for the precipitation-dissolution cycles, was probably needed for all the precipitates to gather in a compact form in the mini-column (the filtration unit); and/or (b), because of the effect of the reduced analyte mass transport to the nebuliser. A higher flow rate than the optimum could have caused a decrease in the sensitivity of calcium: (a), because the extent of the precipitation reaction was
reduced due to the reduced residense time of the reaction mixture; and/or (b), because the minicolumn (the filtration unit) was probably losing precipitate fines. A summary of the observed characteristics of the recorded absorbance profiles as presented in Table 4.6 shows that:

(a), the precipitation reaction was favoured at low flow rates (less than 1 ml min\(^{-1}\)) and the precipitate dissolution was favoured at high flow rates (above 1 ml min\(^{-1}\)); and

(b), high dissolution flows improved the precision and the removal of the aluminium interference as well as offering a stable absorbance base line.

---

**Fig. 4.17.** Selective precipitation of 10 mg l\(^{-1}\) calcium followed by fixed volume dissolution with 5% HCl (aq) in manifold 4.12. Effect of pumping flow rate, ml min\(^{-1}\): (○), 0.44; (△), 0.68; (▲), 0.87; (●), 1.37; and (★), 2.00. Reagent stream was 0.05 M ammonia with 200 mg l\(^{-1}\) ammonium oxalate (AOM).
Table 4.6. Performance of the precipitation manifold (Figure 4.12) at different pumping flow rates

<table>
<thead>
<tr>
<th>criteria.</th>
<th>pumping flow rates, ml min⁻¹:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>below 0.68; ≥ 0.68 and ≤ 1.37; above 1.37.</td>
</tr>
</tbody>
</table>

1. (i), precipitation effluent for 10 mg l⁻¹ calcium: absent. 0.005 abs. 0.010 abs.

(ii), absorbance of 10 mg l⁻¹ calcium in water stream without reagent: 0.020 abs. 0.030 abs. ≥ 0.040 abs.

2. 2nd serial elution of 39 µl of 5% HCl: remnant of 0.02 abs. negligible. negligible.

3. stability of absorbance base line: depressed at ≥ 1 hour operation. stable. stable.

* 4. absolute precision: * 0.020 abs. ≤ 0.010 abs. ≤ 0.005 abs.

* precision of 3 peaks from replicate injection cycles; conventional aspiration of 10 mg l⁻¹ calcium showed 0.010 absorbance noise.

4.4.3. (ii) Effect of sample volume; and (iii) Effect of the filter material

The optimum pumping flow rate of 1.37 ml min⁻¹ as well as higher flow rates were used to study other physical parameters of the manifold in Fig. 4.12.

Procedure and results -- The manifold shown in Fig. 4.12 was used and the water carrier stream was merged with the buffer stream, each pumped at 1.26 ml min⁻¹. The composition of the buffer was 0.05 M ammonia with 50 mg l⁻¹ AOM, which were the optimum conditions from the results of experiments 4.4.2.(ii) and 4.4.3.(iii). Micro-volumes of 39 µl were injected into the water stream for the
precipitation-dissolution cycles. The injection cycle was replicated three times for each test solution (10 mg l$^{-1}$ calcium with 0 to 200 mg l$^{-1}$ aluminium) and the absorbances were recorded at 120 s cm$^{-1}$. The entire procedure was repeated with double serial 39 µl injections for the precipitation stage (78 µl sample volume) and a single 39 µl injection of 5% HCl was used to dissolve the precipitates. The injections of 105 and 210 µl volumes were carried out with an additional valve incorporated just before the valve used to inject the 39 µl volumes of the acid. The experiments were carried out at room temperature and the results are shown in Fig. 4.18.

![Fig. 4.18](image_url)

**Fig. 4.18.** Selective precipitation of 10 mg l$^{-1}$ calcium followed by dissolution with 39 µl of 5% HCl in manifold 4.12. Effect of injected sample volume: ( ), 39 µl; ( ), 78 µl; ( ), 105 µl; and ( ), 210 µl. Reagent stream was 0.05 M ammonia with 50 mg l$^{-1}$ ammonium oxalate; and the pumping rate was 2.53 ml min$^{-1}$.

**Conclusions and results** -- The injection of sample volumes greater than 78 µl (by either serial multiples of 39 µl or single injection) into the manifold showed absorbance peaks for the precipitation effluents of 10 mg l$^{-1}$ calcium, which increased as the injected sample volume increased. However, the filtered precipitates, dissolved with a single 39 µl injection of 5% HCl, showed absorbance
peaks which increased in proportion to the injection volume (up to 105 μl) for samples with low amounts of the aluminium interferent only. The filtration and the mixing capacity of the minicolumn was exceeded on the injection of 210 μl volumes, hence the haphazard absorbances for the eluted calcium.

The absorbances were not significantly affected when a filter (Nylon Acrodisc, 0.45 μm pore-size and 13 mm filter diameter) was fitted to the end of the minicolumn with the aim of improving the collection of the precipitates. This could be due to a reduction in the precipitation reaction for large volumes of sample or loss of precipitate fines by the filter unit.

The reduced sensitivity with increased amount of the interferent, on the injection of 105 μl volumes was investigated as to the reaction role of aluminium in the manifold. The injection sequences for the precipitation-dissolution procedures as applied for calcium were used for the determination of aluminium in the test solutions. The spectrometer was operated at the conditions for the determination of aluminium at maximum sensitivity as in Table 4.7.

**Table 4.7. Optimum conditions for the determination of aluminium with Baird-Atomic, Model A3400, spectrometer.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>wavelength, nm</td>
<td>309</td>
</tr>
<tr>
<td>slit width, nm</td>
<td>0.5</td>
</tr>
<tr>
<td>lamp current, mA</td>
<td>5.</td>
</tr>
<tr>
<td>supporting gas/ flow rate, l min⁻¹</td>
<td>nitrous oxide/ 6.8</td>
</tr>
<tr>
<td>fuel gas/ flow rate, l min⁻¹</td>
<td>acetylene/ 6.8</td>
</tr>
<tr>
<td>burner height, cm</td>
<td>2</td>
</tr>
<tr>
<td>read out</td>
<td>direct</td>
</tr>
<tr>
<td>scale expansion</td>
<td>1</td>
</tr>
<tr>
<td>curve correction</td>
<td>linear</td>
</tr>
<tr>
<td>damping</td>
<td>off</td>
</tr>
<tr>
<td>impact bead</td>
<td>optimum*</td>
</tr>
<tr>
<td>capillary tip adjustment</td>
<td>optimum*</td>
</tr>
</tbody>
</table>

* manufacturer's reference
The calibration graph for aluminium was linear in the range 0 to 50 mg l\(^{-1}\) with a characteristic concentration of 1.47 mg l\(^{-1}\) (the manufacturer's reference value was 1 mg l\(^{-1}\) per 0.0044 abs.). The absorbances from the conventional aspiration of the test solutions (0 to 200 mg l\(^{-1}\) aluminium each with 10 mg l\(^{-1}\) calcium) increased in rough proportion to the concentration of aluminium. But these absorbances were depressed compared with the absorbances for the corresponding simple aluminium solutions as shown in Fig. 4.19.

![Absorbance vs Concentration Graph](image)

**Fig. 4.19.** Effect of aluminium on the precipitation of 10 mg l\(^{-1}\) calcium in manifold 4.12. 
(\(\Delta\)), Precipitation effluents of 39 \(\mu\)l injections monitored for aluminium; and compared with conventional aspirations of (\(\times\)), test solutions; and (\(\bullet\)), standards. 
Reagent stream was 0.05 M ammonia with 50 mg l\(^{-1}\) ammonium oxalate; the nebuliser liquid uptake rate was 6.7 ml min\(^{-1}\) and the pumping rate was 2.53 ml min\(^{-1}\).

The injection of 39 \(\mu\)l volumes of the test solutions and the standards into the manifold showed absorbances for the precipitation effluents but no elution signals with the injection of 39 \(\mu\)l of 5% HCl. Therefore aluminium was not precipitated by the reagent (0.05 M ammonia with 50 mg l\(^{-1}\) ammonium oxalate). Also, aluminium was apparently not retained by the glass beads because the absorbance trend of the precipitation effluents was similar to the absorbances of 39 \(\mu\)l sample injections into water stream without reagent.
The possibility of adsorption of trace amounts of aluminium by the beads, however, was not ruled out, the reason being that the determination of aluminium by flame AAS has the demerit of low sensitivity. This could render significant interference levels of aluminium undetected. Therefore, the packings of glass beads were replaced with polymer material to remove the possible adsorptive effect.

The results for the selective precipitation of $10 \text{ mg} \text{l}^{-1}$ calcium from the test solutions ($10 \text{ mg} \text{l}^{-1}$ calcium with 0 to 200 mg l$^{-1}$ aluminium) when the minicolumn was packed with glass beads and then with polystyrene granules are plotted in Fig. 4.20. All manifold conditions such as flow rate and injection volume, as well as the precipitation- dissolution procedure, were identical for both packings.

![Graph](image)

**Fig. 4.20.** Selective precipitation of $10 \text{ mg} \text{l}^{-1}$ calcium followed by dissolution with 39 µl of 5% HCl in manifold 4.12. Effect of packed filter material in the minicolumn: (○), glass beads; (■), polystyrene granules. Reagent stream was 0.05 M ammonia with 50 mg l$^{-1}$ ammonium oxalate (AOM); and the pumping flow rate was 1.37 ml min$^{-1}$. (●), interference curve for calcium, in water streams without reagent at 22 °C.

There was a complete removal of the aluminium interference with both materials and the polystyrene granules offered a better precision (average RSD: 4% for granules...
and 10% for beads) but with reduced sensitivity. The packing of the granules was less compact than the beads, due to their irregular shape. This could reduce the mixing of reactants as well as increase the loss of precipitate fines. However, a single injection of 39 µl 5% HCl eluted all calcium ions from the polymer granules whereas the glass beads required a second or third injection act to clear the remnant absorbance due to the adsorbed calcium ions. The polymer material was, therefore, a better filter.

Further experiments were designed to study the effect of physical parameters such as pumping flow rate, size of minicolumn, size of granules, and length of tube traversed by the sample for the minicolumn of polystyrene granules. The manifold shown in Fig. 4.12 was used. Each adjustment was carried out whilst all other parameters of the manifold were kept constant. The results showed the following: (a), the sensitivity of the elution signals increased as the pumping flow decreased such that the absorbance doubled at 0.68 ml min⁻¹ in comparison to 1.37 ml min⁻¹. Further decrease to 0.4 ml min⁻¹ reduced the absorbance; and (b), the length of the minicolumn when reduced from 7.5 cm to 3 cm, the use of granules with diameter less than 0.5 mm to pack the column, and the extension of the tube length (from the valve to the Y-confluence piece) from 15 cm to 2 m did not significantly affect the absorbances at 1.37 ml min⁻¹.

4.4.3. (iv) Effect of packed confluence mixers

The precipitation reaction of calcium with ammonia-ammonium oxalate required improved mixing as well as more contact time to offer high sensitivity. This was effected in the manifold with the use of a confluence piece which was designed to offer improved mixing of the merging streams. The merging point of the glass Y-piece, used as the confluence piece, was blown oval in shape to contain a hold-up volume of liquid of about 2 ml. The Y-piece was positioned upside down in the manifold so that the vertical arm served as the inlet of the sample stream. The arm was fabricated to dip (about 1 mm) into the hold-up volume of liquid. This arrangement permitted an additional radial diffusion of the sample zone, as well as the axial diffusion afforded with stream segmentation which was earlier observed in section 4.4.2.(iv).

Procedure and results -- The manifold shown in Fig. 4.12 was used. The minicolumn (filtration unit), however, was packed with polystyrene granules, diameter less than 0.5 mm. The glass Y-piece had its merging point blown oval in
shape and contained three polystyrene granules (diameter 3 mm) which could move freely when liquid flowed. The pump tube with internal diameter 0.25 mm, was used to deliver the reagent stream and a 0.4 mm diameter pump tube was used for the water stream. Firstly, the absorbance profiles for 39 µl injections of 10 mg l⁻¹ calcium into water streams, without reagent, were recorded at 120 s cm⁻¹ for different settings of the pump head rotation speed control. The residence times for the peaks were obtained from the chart recordings and used for the precipitation stage of the samples. Two minutes wash was added to the residence times for the precipitation- dissolution cycles for each pumping flow rate. Secondly, the sequences for the precipitation- dissolution of two test solutions (10 mg l⁻¹ Ca with and without 200 mg l⁻¹ aluminium) were carried out at different settings of the pump which corresponded to flow rates from 0.1 to 1.5 ml min⁻¹. The reagent was 0.05 M NH₃ with 50 mg l⁻¹ AOM. The precipitates were dissolved with 5% HCl using 39 µl sample loop. All absorbances were recorded at 120 s cm⁻¹.

The entire procedure was repeated for three similar confluence mixers that contained: (a), three "free moving" glass beads; (b), loose packings of glass beads; and (c), loose packings of glass helixes. The diameter of the packed entities was 3 mm. The results are presented in Table 4.8.

Conclusions and comments -- The absorbance of calcium, from the dissolved precipitates, increased as the flow rate decreased; and the aluminium interference was removed for 200 mg l⁻¹ except at very low flow rates (less than 0.5 ml min⁻¹ total flow) for all the confluence mixers. The loose packings of glass helixes and beads afforded higher absorbances whilst the helixes afforded better removal of interference than the mobile beads or granules especially at low flow rates. This showed that mixing was improved at the merging point. The increased absorbance at reduced pumping flows again showed the need for more contact time for the calcium/oxalate precipitation process.

In the experiments, the mobile beads had the disadvantage that they could block the stream outlet and cause leaks in the manifold. This was prevented with a gentle tap on the Y- piece at intervals. Air pockets could also cause reduced and imprecise absorbances and eventual leaks in the manifold if allowed to build up. The Y- piece was flushed with a high flow liquid stream to eliminate the air pockets at the start of each experimental run. However, tiny bubbles if carried along with the stream, had no significant effect on the absorbances because they were nullified at the merging point for air compensation.
Fig. 4.21. Two-line manifold for the continuous precipitation, filtration and dissolution with fixed volume elution, for calcium. C, water carrier; R, ammonia- ammonium oxalate reagent; Pc, precoil; Ps, pulse damper; I, injection point; Y, confluence mixer; Rc, reaction coil (50 cm long, 0.58 mm i.d.); f, membrane filter; v, 2-way stream switching valve; and a, air compensation inlet through omnifit tee.

In-house packing of an on-line filter: 1, end connector; 2, "O" ring; 3, coupling connector; 4, disc filter; and 5, omnifit tee.

A membrane filter to retain precipitates, as shown in Fig. 4.21. The polymer filters (Gelman disposable syringe filters) were contained in polypropylene housings and were each fitted into the manifold with PTFE luer locks, resin glued to prevent leaks. The stainless steel disc filter (used for stream cleaning in HPLC) was packed in-house (see insert in Fig. 4.21) and fitted into the manifold. The volume of the injection loop was 39 μl and the reagent was 0.05 M NH₃ with 50 mg l⁻¹ AOM. The procedural sequences of experiment 4.4.3.(iv) were applied as the pumping flow rates were varied for the injection of the test solutions (10 mg l⁻¹ Ca with 0 to 1000 mg l⁻¹ aluminium). A 5% HCl solution was used to dissolve the precipitate.
The results are shown in Table 4.9 and the performance of the different filters in the manifold are summarised in Table 4.10.

### Table 4.9. Effect of membrane filters on the absorbance of 10 mg l\(^{-1}\) calcium using the manifold in Fig. 4.21.

<table>
<thead>
<tr>
<th>[Al] (\text{mg l}^{-1})</th>
<th>0.67 ml min(^{-1})</th>
<th>1.02 ml min(^{-1})</th>
<th>1.54 ml min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>STAINLESS STEEL disc:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 (\mu)m pore-size, 5 mm filter diameter and 2 mm thick.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.153 ± 0.003</td>
<td>0.160 ± 0.010</td>
<td>0.143 ± 0.008</td>
</tr>
<tr>
<td>200</td>
<td>0.137 ± 0.004</td>
<td>0.162 ± 0.002</td>
<td>0.146 ± 0.010</td>
</tr>
<tr>
<td>300</td>
<td>0.135 ± 0</td>
<td>0.176 ± 0.001</td>
<td>0.130 ± 0</td>
</tr>
<tr>
<td>400</td>
<td>0.123 ± 0</td>
<td>0.164 ± 0.009</td>
<td>0.138 ± 0.001</td>
</tr>
<tr>
<td>500</td>
<td>0.128 ± 0.003</td>
<td>0.157 ± 0.007</td>
<td>0.153 ± 0.003</td>
</tr>
<tr>
<td>700</td>
<td>0.123 ± 0.001</td>
<td>0.137 ± 0.004</td>
<td>0.130 ± 0</td>
</tr>
<tr>
<td>1000</td>
<td>0.110 ± 0</td>
<td>0.100 ± 0.010</td>
<td>0.090 ± 0.010</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[Al] (\text{mg l}^{-1})</th>
<th>0.94 ml min(^{-1})</th>
<th>1.42 ml min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>NYLON Acrodisc (PN 4438):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.45 (\mu)m pore-size, 25 mm filter diameter and fluid retention, 100 (\mu)l.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0.099 ± 0.001</td>
<td>0.099 ± 0.004</td>
</tr>
<tr>
<td>200</td>
<td>0.099 ± 0.001</td>
<td>0.102 ± 0.004</td>
</tr>
<tr>
<td>400</td>
<td>0.099 ± 0.001</td>
<td>0.102 ± 0.002</td>
</tr>
<tr>
<td>500</td>
<td>0.088 ± 0.008</td>
<td>0.100 ± 0.006</td>
</tr>
<tr>
<td>700</td>
<td>0.088 ± 0.008</td>
<td>0.086 ± 0.004</td>
</tr>
<tr>
<td>1000</td>
<td>0.075 ± 0.001</td>
<td>0.084 ± 0.004</td>
</tr>
</tbody>
</table>
Table 4.9 continued

(III), NYLON Acrodisc (PN 4426):
0.45 μm pore-size, 13 mm filter diameter and fluid retention, 28 μl.

<table>
<thead>
<tr>
<th>[Al] μ</th>
<th>absorbance of Ca at total pumping flow rates:</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg l⁻¹</td>
<td>0.62 ml min⁻¹</td>
</tr>
<tr>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>0</td>
<td>0.181 ± 0.007</td>
</tr>
<tr>
<td>100</td>
<td>0.182 ± 0.006</td>
</tr>
<tr>
<td>200</td>
<td>0.190 ± 0.010</td>
</tr>
<tr>
<td>300</td>
<td>0.182 ± 0.017</td>
</tr>
<tr>
<td>500</td>
<td>0.180 ± 0.020</td>
</tr>
<tr>
<td>700</td>
<td>0.159 ± 0.019</td>
</tr>
<tr>
<td>1000</td>
<td>0.179 ± 0.009 *</td>
</tr>
</tbody>
</table>

(IV), PTFE Acro LC 35 (PN 4440):
0.45 μm pore-size, 5 mm filter diameter and fluid retention, 0 μl.

<table>
<thead>
<tr>
<th>[Al] μ</th>
<th>absorbance of Ca at total pumping flow rates:</th>
</tr>
</thead>
<tbody>
<tr>
<td>mg l⁻¹</td>
<td>0.32 ml min⁻¹</td>
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<tr>
<td>↓</td>
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</tr>
<tr>
<td>0</td>
<td>0.183 ± 0.002</td>
</tr>
<tr>
<td>100</td>
<td>0.204 ± 0.014</td>
</tr>
<tr>
<td>200</td>
<td>0.199 ± 0.013</td>
</tr>
<tr>
<td>300</td>
<td>0.188 ± 0.018</td>
</tr>
</tbody>
</table>

Absorbances were the mean of 5 peak heights.
(-) were undetermined due to leaks in the manifold.
* wash increased from 5 minutes to 15 minutes.
Table 4.10. Performance of membrane filters using the manifold in Fig. 4.21.

<table>
<thead>
<tr>
<th>Filter type</th>
<th>Characteristics in the manifold</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I), stainless steel disc, 2 μm pore-size, 5 mm f.d., and 2 mm thick.</td>
<td>0.18 absorbance for 10 mg l⁻¹ calcium at 1 ml min⁻¹, no back pressure excess, degassing of streams from 1.5 ml min⁻¹, 10 : 700 Ca : Al tolerated at ≤ 5 min wash⁻¹.</td>
</tr>
<tr>
<td>(II), nylon membrane, 0.45 μm pore-size, 25 mm f.d.</td>
<td>0.1 absorbance for 10 mg l⁻¹ calcium at 1.5 ml min⁻¹, no back pressure excess, degassing of streams from 2 ml min⁻¹, 10 : 500 Ca : Al tolerated at ≤ 5 min wash⁻¹.</td>
</tr>
<tr>
<td>(III), nylon membrane, 0.45 μm pore-size, 13 mm f.d.</td>
<td>0.18 absorbance for 10 mg l⁻¹ calcium at 0.6 ml min⁻¹, back pressure excess from 1 ml min⁻¹, 10 : 300 Ca : Al tolerated at ≤ 5 min wash⁻¹.</td>
</tr>
<tr>
<td>(IV), PTFE membrane, 0.45 μm pore-size, 5 mm f.d.</td>
<td>0.2 absorbance for 10 mg l⁻¹ calcium at 0.3 ml min⁻¹, back pressure excess from 0.3 ml min⁻¹, 10 : 200 Ca : Al tolerated at ≤ 5 min wash⁻¹.</td>
</tr>
</tbody>
</table>

Conclusions and comments -- The incorporation of membrane filters into the manifold caused a pressure build-up that produced recurrent leaks during the experiments. The leakage became worse as the hold-up volume and/or the surface area of the filter reduced and it was especially aggravated for the hydrophobic PTFE membrane. The PTFE membrane had to be flushed with ethanol to permit the few readings to be recorded. The pressure build-up also became worse as the pumping flow rate increased, an effect that forced the precipitate fines to clog the filter pores and cause the degassing of the liquid streams. The pores were so clogged that the filters had to be washed in an ultrasonic bath once a leakage occurred. The stainless steel filter when packed tightly (with negligible liquid hold-up volume) caused excessive pressure build-up that gave leaks in the manifold. This defect was reduced when o-rings of reasonable thickness (about 1 mm) were used in the filter assembly. All the filter units when being fitted into the manifold first had their
nebuliser end connection open for the liquid to stream freely and flush out air pockets before their final connection. This reduced the incidence of dead volumes which could retain some acid and so cause base line absorbance spikes. The absorbance spikes resulted from the premature stripping of calcium by the pockets of acid, during the precipitation periods of the injection cycles. These problems notwithstanding, the use of a suitable polymer membrane filter permitted the removal of a high proportion of the aluminium interferent. The reason was that the controlled pore-size of the membrane permitted an extended wash time without a significant loss of calcium. The sensitivity of calcium decreased as the filter area/retention volume increased.

The NYLON acrodisc, P/N 4426 filter unit with, 0.45 μm pore-size and 13 mm diameter was later used for the determination of calcium in cement because: (a), it gave higher sensitivity than the stainless steel or the filter of 25 mm diameter; and (b), it permitted a long wash of the precipitates without causing excessive pressure which offered improved removal of aluminium interference than PTFE. The column of polystyrene granules, when fitted with a PTFE membrane filter (0.2 μm pore, 5 mm filter diameter) at its outlet, could also gather precipitates with minimal back pressures in the manifold. The application of the manifolds, which incorporate these filter units, to determine calcium in cement will be described later in section 4.5.

4.4.4. Discussion

In the literature, oxalate precipitation is used for the gravimetric determination of calcium in the presence of various interferents such as aluminium, iron, silicate and phosphate.29-31 The precipitation reaction is quantitative above pH 4, hence careful pH control readily eliminates the potential interferents either as cations or anions. In the batch procedure, the analysis had always been tedious, time consuming, as well as requiring an hour or more of heating the reaction mixture. However, trace amounts of ammonium oxalate (mg l\textsuperscript{-1} levels) with a large excess of ammonia (≥ 0.05 M) could selectively precipitate calcium without heating as demonstrated with the use of the manifolds in Figures 4.12 and 4.21. The use of ammonium oxalate reagent, either in neutral or acidic medium, even on heating, failed to effect a significant precipitation in a two-line manifold. Hence the acidity of the sample matrix had to be minimum, at below the buffer capacity of the reagents, to permit precipitation in the designed manifolds (see Fig. 4.16(I)). The application of a suitably designed manifold to deduce the equilibrium constant for the precipitation reaction will be presented later, in Chapter 5.
The kinetics of the precipitation reaction of calcium with oxalate ions was sufficiently slow that the reactants had to be in continuous contact (gauged by the residence times of the reaction zone) for two minutes or more to improve sensitivity. The operation of the manifold at low pumping flow rates of less than 1 ml min\(^{-1}\) (see Fig. 4.9) was preferred to stopped-flow with high flow rate because the residence time and the dispersions/mixing of the reaction system could be increased concurrently in the manifolds. The merging streams manifolds (see Fig. 4.12 and Fig. 4.21) offered reproducible and selective precipitations without the manifold reaction having attained a steady state. This is an advantage of an FIA system. Thus the depressive effect of 1000 mg l\(^{-1}\) aluminium present in a test solution with 10 mg l\(^{-1}\) calcium could be removed at 1.4 ml min\(^{-1}\) with a nylon membrane filter (see Table 4.9.(II)) if selectivity rather than sensitivity was the critical feature for the candidate analysis. The precipitates readily clogged the pores of membrane filters (see Table 4.10) unless the filters were preceded by a packed bed. The packed bed with membrane filter offered a graded collection of precipitates that probably prevented the formation of 'cake' on the membrane.

In the experiments, prolonged pumping of solutions to the nebuliser caused the absorbance baseline to shift at pumping rates below 1 ml min\(^{-1}\). The base line was restored to normal after aspirating water to wash the nebuliser. Therefore a better manifold design should divert precipitation effluents from the nebuliser and permit the aspiration of water to maintain thermal equilibrium in the nebuliser-burner system in the interim. Attempts to divert the precipitation effluents to waste by the incorporation of the filter unit within the injection loop of a 4-way, low pressure, rotary valve (Rheodyne 5041) failed due to the build up of precipitates in the conduits. The result was an excessive back pressure that produced immediate leaks in the manifold. A stream selection valve located after the filter unit was a better option.

The precipitation of calcium oxalate in a continuous mode in FI-AAS was reported by Valcarcel and coworkers.\(^{19,28}\) The precipitation reaction of the calcium ions with ammonium oxalate was effected with stopped-flow FIA with heating in the presence of acetic acid - sodium acetate buffer. The manifold devised by the authors was for continuous filtration with and without precipitate dissolution. The determination of oxalate ions with the use of the manifold, without precipitate dissolution, was reported to offer more precise results (5% RSD) than the use of the manifold with precipitate dissolution (9% RSD).\(^{19}\) The authors' report and this work agree on: (a), the slow kinetics of the calcium/oxalate reaction; and (b), the crystalline
precipitates of calcium oxalate readily clog membrane filters. However, the peak height quantification with the use of membrane filters (see Table 9), in this report, showed improved precision as sensitivity increased. The absorbances were as precise as 2% RSD for high peaks. This improvement occurred when low flow rates (1 ml min$^{-1}$ or less) were used to increase the residence time of the reaction mixture. This, in turn, increased the extent of the precipitation reaction. A further observation was that a simple Y-piece and a mixing coil could not adequately produce the homogeneous mixing required to increase extent of the precipitation of calcium oxalate, the reason being that the peristaltic pump pulses caused the solutions to segment each other. At low pumping rates, the length of the segments increased and the diffusion amongst segments was not complete though the increased residence time favoured the reaction. Similar observations on the inadequacy of simple tees with mixing coils in flowing streams have been contained in some recent literature reports. Therefore, manifold designs with tees and reaction coils, that use the sole mutual dispersions of a sample into a carrier reagent to effect mixing in the manifold, would tend to offer poor sensitivity and in turn poor precision. These analytical characteristics would be specifically shown by calcium/oxalate and other similar precipitation reactions of slow kinetics. The manifolds reported by Valcarcel and coworkers used the sole mutual dispersions of the reactants for mixing, hence the poor precision realised. In this work, a confluence piece with a hold up volume could offer up to 40% improved mixing (see Table 4.8(I)). In addition, the incorporation of air compensation into the manifolds (absent in the works of Valcarcel and coworkers) reduced the chances of air bubbles to cause imprecise results in absorbance peak height quantification. The uniform ingress of air at the T-piece for air compensation nullified the erratic effect of these bubbles. Air bubbles are often unnoticed visually in the flowing streams.

4.4.5. Conclusions

On-line selective precipitation of calcium as the basic oxalate in FI-AAS removed the depressive effect of aluminium on the absorbance of calcium. Up to 1000 mg l$^{-1}$ aluminium in 10 mg l$^{-1}$ Ca solution could be removed. The effective reagent was a high concentration of ammonia ($\geq 0.05$ M) with a trace concentration of ammonium oxalate ($\leq 200$ mg l$^{-1}$).

The precipitation process was favoured by low pumping flow rates (less than 1 ml min$^{-1}$). The dissolution of the precipitates with relatively high flow rates (greater
than 1 ml min\(^{-1}\) of the solvent favoured sharp peaks with the possibility of increased sensitivity.

The design of the merging stream manifold required:
(a), a filtration device of 'graded' pore-size (packed bed with membrane filter at its outlet) to collect precipitates, permit washing of the precipitates and subsequent dissolution of the precipitates without excessive back pressures that could cause manifold leaks; and
(b), an efficient mixer (confluence piece with retention volume) to improve sensitivity.

4.5. DETERMINATION OF CALCIUM IN CEMENT

Two different forms of commercial cement were analysed, White Portland Cement (WPC), supplied by Blue Circle Cement PLC, and Ordinary Portland Cement (OPC), supplied by Ketton Cement Co. Ltd. The samples had been previously analysed for their surface compositions in the Chemistry laboratory at Loughborough University by Ball and Simmons.\(^{33}\) The bulk compositions of the anhydrous cement samples were provided by the suppliers, as shown in Table 4.11.

| Table 4.11. Bulk composition of two different forms of commercial cement. |
|--------------------------|--------------------------|--------------------------|
| element                  | White Portland Cement    | Ordinary Portland Cement |
|                          | atom % (\(^{m/M}\) %)     | atom % (\(^{m/M}\) %)     |
| calcium                  | 31.2 (49.5)               | 29.1 (46.1)               |
| aluminium                | 2.2 (2.3)                 | 3.1 (3.3)                 |
| iron                     | 0.1 (0.2)                 | 1.0 (2.2)                 |
| magnesium                | ND                       | 1.03 (0.1)                |
| sulphur                  | 0.66 (0.1)                | 0.64 (0.1)                |
| sodium/potassium         | 1.0 (1.5)                 | 1.13 (1.7)                |
| silicon                  | 9.6 (10.7)                | 8.6 (9.6)                 |
| oxygen                   | 55.20 (34.9)              | 55.7 (35.2)               |

ND, the element was not determined.
4.5.1. Sample dissolution

The samples of cement were dissolved by the hydrofluoric acid-boric acid method in an ultrasonic bath. The dissolution stages for each sample were carried out in a fume cupboard:

(a) a few milligrams (5 - 15 mg) of the well mixed powdered sample were weighed into a clean, dry and weighed 150 ml polythene bottle;
(b) three drops of concentrated hydrochloric acid were added followed by 2 ml of reagent water; the bottle was placed in an ultrasonic bath for 5 minutes until all the particles had dissolved (the solution of WPC was colourless and that of OPC was greenish-brown, due to its higher percentage of iron. There were glassy flakes in the solutions due to precipitated silica.);
(c) three drops of hydrofluoric acid (40%) were added to the solution with a further 5 minutes in the ultrasonic bath to dissolve the silica;
(d) one gram of boric acid (H$_3$BO$_3$ (s)) was added to react with the excess hydrofluoric acid and to permit the use of glass volumetric flasks. The ultrasonic bath was operated for 2 minutes to dissolve the solids.

The polythene bottle was removed from the bath, wiped dry on the outside and the solution made up to 100 g with reagent water (by the method of weighing by difference). The stock solution was stored with the polythene bottles tightly stoppered.

Stock solutions for each type of cement were prepared in duplicates and a blank was prepared by an identical dissolution procedure but without the sample. These solutions as prepared were further diluted (dilution factor of 10) for the absorbances to fall within the linear range of the calibration graphs.

4.5.2. Calibration procedures

The normal calibration procedure for on-line precipitation was carried out with the standard solutions of calcium (1 - 12 mg l$^{-1}$ Ca) and the sample solutions of cement. The spectrometer was operated with the conditions for the determination of calcium at maximum sensitivity as shown earlier in Table 4.2. The nebuliser liquid uptake rate with the settings was 8.0 ml min$^{-1}$. The manifold that incorporated the confluence mixer (packed with glass helixes), the reaction coil and the nylon membrane filter (0.45 μm pore-size, 13 mm filter diameter) as shown in Fig. 4.22 was used. The pump tubes for the water carrier, reagent (0.05 M NH$_3$ with 50
Fig. 4.22. Two-line manifold for the continuous precipitation, filtration and dissolution with stream elution, for calcium. C, water carrier; R, ammonia-ammonium oxalate reagent; Pc, precoil; Ps, pulse damper; I, injection point; Y, confluence mixer; Rc, reaction coil (50 cm long, 0.58 mm i.d.); f, membrane filter; v1 and v2, 2-way stream switching valves; a, air compensation inlet; and T, T-connector.

mg l⁻¹ AOM) and acid (5% HCl) streams were of internal diameters, 0.4 mm, 0.4 mm and 2.05 mm, respectively. The pump control was set such that the pumping flow rates for the water, reagent and acid streams were 0.43, 0.36 and 0.83 ml min⁻¹, respectively. These flow rates offered 0.8 ml min⁻¹ for the precipitation stage and 1.26 ml min⁻¹ for the dissolution stage of the following procedure:
Water and reagent were pumped for 2 minutes to equilibrate the the confluence mixer, the reaction coil and the filter whilst acid stream was diverted back to the reservoir. Injections of 39 µl of the blank solution were made and after a 6 minutes delay for each injection, acid was pumped to give the blank absorbance that was recorded at 120 s cm⁻¹. The precipitation-dissolution cycle (about 7 minutes for the cycle) was carried out three times for the blank. The operation sequences were repeated for each of the standards starting with the smallest concentration and finishing with the sample solutions of cement. The entire procedure was repeated in turn for 80 µl and 150 µl injection volumes.

The precipitation-dissolution cycles were repeated five times for the injection of 39 µl of the blank solution with the spectrometer operated on a scale expansion of ten. These absorbances were used to calculate the detection limit for the manifold.

Water was pumped in all channels for 15 minutes before the manifold operation was closed down.

For the comparative study, the blanks, standards and sample solutions were aspirated conventionally, with and without the addition of 5 ml, 1% (m/v) lanthanum chloride in 5 M HCl. The lanthanum solution was added to the aliquots of the stock solutions in 50 ml standard flasks during dilution. The absorbances were recorded at 120 s cm⁻¹. Also, for the comparative study, the manifold in Fig. 4.22 was further adjusted such that the reaction coil and the nylon membrane filter were replaced with the minicolumn of polystyrene granules and a PTFE membrane filter, 0.2 µm pore-size and 5 mm filter diameter. The manifold was operated with the injection of 50 µl volumes using the conditions and similar sequences of the precipitation-dissolution cycles as described earlier for the normal calibration procedure.

The results of these experiments are shown in Table 4.12 and Figs. 4.23 to 4.25.
Table 4.12. Results of the normal calibration procedure for the precipitation manifold and conventional aspiration

(A), FI-AAS:

<table>
<thead>
<tr>
<th>solution</th>
<th>mg l⁻¹ Ca</th>
<th>Absorbance</th>
<th>% RSD</th>
<th>Absorbance</th>
<th>% RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(I), 39 µl injection</td>
<td></td>
<td>(II), 80 µl injection</td>
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</tr>
<tr>
<td>blank</td>
<td>0</td>
<td>0.007 ± 0.003</td>
<td>&gt; 16</td>
<td>0.013 ± 0.001</td>
<td>8</td>
</tr>
<tr>
<td>1</td>
<td>1.0</td>
<td>0.019 ± 0.003</td>
<td>16</td>
<td>0.038 ± 0.004</td>
<td>11</td>
</tr>
<tr>
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<td>0.036 ± 0.001</td>
<td>3</td>
<td>ND</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>4.0</td>
<td>0.063 ± 0.005</td>
<td>8</td>
<td>0.083 ± 0.006</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>6.0</td>
<td>0.091 ± 0.004</td>
<td>4</td>
<td>0.154 ± 0.010</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>8.0</td>
<td>0.110 ± 0.004</td>
<td>4</td>
<td>0.184 ± 0.002</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>10.0</td>
<td>0.130 ± 0.005</td>
<td>4</td>
<td>0.279 ± 0.016</td>
<td>6</td>
</tr>
<tr>
<td>7</td>
<td>12.0</td>
<td>ND</td>
<td></td>
<td>0.237 ± 0.005</td>
<td>2</td>
</tr>
<tr>
<td>WPC (1)</td>
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<td>0.042 ± 0.003</td>
<td>7</td>
<td>0.154 ± 0.010</td>
<td>7</td>
</tr>
<tr>
<td>WPC (2)</td>
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<td>0.040 ± 0.003</td>
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<td>0.184 ± 0.002</td>
<td>1</td>
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<tr>
<td>OPC (1)</td>
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<td>ND</td>
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<tr>
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<td>ND</td>
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<tr>
<td></td>
<td></td>
<td>(III), 150 µl injection</td>
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<td>(IV), 50 µl injection</td>
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<td>1.0</td>
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<td>2.0</td>
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<td>&lt; 1</td>
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<td>4.0</td>
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<td>0.195 ± 0.007</td>
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<td>0.118 ± 0.002</td>
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<td>0.154 ± 0.010</td>
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<td>0.124 ± 0.007</td>
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<td>0.184 ± 0.002</td>
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<td>6</td>
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<td></td>
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<tr>
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<td>0.013 ± 0.001</td>
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<td>1.0</td>
<td>ND</td>
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<td>0.038 ± 0.004</td>
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<td>0.028 ± 0.003</td>
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<td>0.154 ± 0.010</td>
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<td>0.235 ± 0.005</td>
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<td>8</td>
<td>15.0</td>
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</tr>
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<td>30.0</td>
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Table 4.12 continued

<table>
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<tr>
<th></th>
<th>WPC (1)</th>
<th>WPC (2)</th>
<th>OPC (1)</th>
<th>OPC (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.248 ± 0.025</td>
<td>0.205 ± 0.005</td>
<td>0.180 ± 0.020</td>
<td>0.116 ± 0.005</td>
</tr>
<tr>
<td>(I) - (III),</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| on-line reaction coil with NYLON membrane filter, 0.45 µm pore, 13 mm f.d.  
| and (IV),      |          |         |         |         |
| on-line minicolumn of polymer granules with PTFE membrane filter; 0.2 µm pore, 5 mm f.d.  
| ND,            |          |         |         |         |
| solutions were not injected.  
| ALL absorbances were the mean of 3 to 5 peak heights.  |

(B), Conventional AAS:

<table>
<thead>
<tr>
<th>solution</th>
<th>mg l⁻¹ Ca</th>
<th>Absorbance</th>
<th>% N: S</th>
<th>Absorbance</th>
<th>% N: S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>without lanthanum</td>
<td>with lanthanum (III)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>water</td>
<td>0</td>
<td>0</td>
<td></td>
<td>0.012 ± 0</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>blank</td>
<td>0</td>
<td>0</td>
<td></td>
<td>0.110 ± 0</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>1</td>
<td>1.0</td>
<td>0.080 ± 0</td>
<td>&lt; 1</td>
<td>0.152 ± 0.002</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>0.150 ± 0.002</td>
<td>1</td>
<td>0.375 ± 0.005</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>5.0</td>
<td>0.345 ± 0.005</td>
<td>1</td>
<td>0.525 ± 0.015</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>7.0</td>
<td>0.470 ± 0.010</td>
<td>2</td>
<td>0.740 ± 0.015</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>10.0</td>
<td>0.630 ± 0.010</td>
<td>2</td>
<td>0.870 ± 0.020</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>12.0</td>
<td>0.725 ± 0.015</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WPC (1)</td>
<td></td>
<td>0.260 ± 0.005</td>
<td>2</td>
<td>0.176 ± 0.002</td>
<td>1</td>
</tr>
<tr>
<td>WPC (2)</td>
<td></td>
<td>0.285 ± 0.005</td>
<td>2</td>
<td>0.185 ± 0.002</td>
<td>1</td>
</tr>
<tr>
<td>OPC (1)</td>
<td></td>
<td>0.320 ± 0.005</td>
<td>2</td>
<td>0.430 ± 0.010</td>
<td>2</td>
</tr>
<tr>
<td>OPC (2)</td>
<td></td>
<td>0.240 ± 0.005</td>
<td>2</td>
<td>0.320 ± 0.005</td>
<td>2</td>
</tr>
</tbody>
</table>

N: S, noise to signal ratio.
Fig. 4.23. (i) Normal working curves for calcium with the spectrometer set for maximum sensitivity. (●), conventional AAS; (○), conventional AAS with lanthanum (III); and (▲), 39 μl injection with precipitation flow of 0.8 ml min⁻¹ and dissolution flow of 1.26 ml min⁻¹.

(ii) Effect of sample volume on normal working curves for calcium by the flow injection method: (▲), 39 μl; (●), 80 μl; and (○), 150 μl injection.

(The nebuliser liquid uptake rate was 8.0 ml min⁻¹ and the manifold incorporated: confluence mixer packed with glass helixes; reaction coil, 50 cm long; and nylon membrane filter, 0.45 μm pore, 13 mm filter diameter.)
Fig. 4.24. Normal working curves for calcium with the spectrometer set for maximum sensitivity. The nebuliser liquid uptake rate was 8.0 ml min\(^{-1}\). (●), conventional AAS; (○), conventional AAS with lanthanum (III); and (■), 50 µl injection with precipitation flow of 0.8 ml min\(^{-1}\) and dissolution flow of 1.26 ml min\(^{-1}\). (manifold incorporated: confluence mixer packed with glass helixes; minicolumn of polystyrene granules; and PTFE membrane filter, 0.2 µm pore, 5 mm filter diameter.)

Fig. 4.25. Recorder tracings of 39 µl injections of blank and calcium standards with a precipitation flow of 0.80 ml min\(^{-1}\) and a dissolution flow of 1.26 ml min\(^{-1}\).
4.5.3. Characteristic concentration, precision and detection limit

The manifold operation with 39 \( \mu l \) injection offered an improved linear range (0 - 10 mg l\(^{-1}\) calcium) over conventional aspiration without lanthanum addition as shown in Fig. 4.23.(i). The characteristic concentration of 0.32 mg l\(^{-1}\) per 0.0044 absorbance for 39 \( \mu l \) injection volume improved to 0.08 mg l\(^{-1}\) for 150 \( \mu l \) injections but with reduced linear range as shown in Fig. 4.23.(ii). The absolute precision of the FI-peak heights was on the average 0.005 absorbance units and the precision became worse for high concentrations of the solute or large injection volumes, as shown in Table 4.12. This could be due to the loss of precipitate fines by the filtration unit and/or the reactants were no longer mixed in reproducible proportions. This precision, calculated as % RSD, improved as the peak height increased, to an average best of 4%. The value is worse than the precision obtained for conventional aspiration which improved as the peak height decreased, to 1% RSD or less. The FI- detection limit, deduced as the concentration that corresponded to three times the standard deviation of the peak heights of the blank (see Fig. 4.25), was 0.25 mg l\(^{-1}\). The value of the detection limit deduced for conventional aspirations was not significantly different.

4.5.4. Accuracy of the results

The stock solutions of the cement samples were diluted such that their absorbances were within the linear range of the calibration graphs. The concentrations of calcium, read off the graphs, were substituted into equation 4.9 to calculate the calcium content of the samples. The results are presented in Table 4.13.

\[
\% Ca = \frac{C_{\text{graph}}}{C_{\text{stock}}} \cdot D \cdot 100
\]

where,
- \( C_{\text{graph}} \) is the concentration derived from the calibration graph, mg l\(^{-1}\);
- \( C_{\text{stock}} \) is the concentration of sample stock solution, mg l\(^{-1}\); and
- \( D \) is the dilution factor.
Table 4.13. Determination of calcium in cement.

(i), curve characteristics

<table>
<thead>
<tr>
<th>method</th>
<th>Regression equation</th>
<th>linear range</th>
<th>corr. coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>normal AAS:</td>
<td>( A = 0.0126 + 0.0722 , C )</td>
<td>0 - 5 mg l(^{-1})</td>
<td>0.998</td>
</tr>
<tr>
<td>AAS + La(III):</td>
<td>( A = 0.0017 + 0.0750 , C )</td>
<td>0 - 12 mg l(^{-1})</td>
<td>0.999</td>
</tr>
<tr>
<td>manifold:</td>
<td>( A = 0.0065 + 0.0141 , C )</td>
<td>0 - 10 mg l(^{-1})</td>
<td>0.999</td>
</tr>
<tr>
<td></td>
<td>( A = -0.0008 + 0.0180 , C )</td>
<td>0 - 10 mg l(^{-1})</td>
<td>0.999</td>
</tr>
</tbody>
</table>

- \( A, \) absorbance peak height;
- \( C, \) concentration of calcium, mg l\(^{-1}\);
- corr. coeff., correlation coefficient;
- \( \dagger \) on-line reaction coil with NYLON membrane filter, 0.45 \( \mu \)m pore, 13 mm f.d.;
- \( \ddagger \) on-line minicolumn of polymer granules with PTFE membrane filter, 0.2 \( \mu \)m pore, 5 mm f.d.

(ii), analysis of White Portland Cement for calcium

<table>
<thead>
<tr>
<th>method</th>
<th>stock, mg l(^{-1})</th>
<th>Absorbance, mg l(^{-1})</th>
<th>graph, % Ca, found</th>
<th>accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>normal AAS:</td>
<td>96.77</td>
<td>0.260 ± 0.005</td>
<td>3.43 ± 0.1</td>
<td>35 ± 1</td>
</tr>
<tr>
<td></td>
<td>102.49</td>
<td>0.285 ± 0.005</td>
<td>3.77 ± 0.10</td>
<td>37 ± 1</td>
</tr>
<tr>
<td>AAS + La(III):</td>
<td>48.34</td>
<td>0.176 ± 0.002</td>
<td>2.32 ± 0.00</td>
<td>48.1 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>51.24</td>
<td>0.185 ± 0.002</td>
<td>2.44 ± 0.00</td>
<td>47.7 ± 0.1</td>
</tr>
<tr>
<td>manifold:</td>
<td>( \dagger ) 39 µl;</td>
<td>51.24</td>
<td>0.042 ± 0.003</td>
<td>2.52 ± 0.25</td>
</tr>
<tr>
<td></td>
<td>48.34</td>
<td>0.040 ± 0.003</td>
<td>2.36 ± 0.25</td>
<td>49 ± 5</td>
</tr>
<tr>
<td></td>
<td>( \ddagger ) 50 µl;</td>
<td>74.70</td>
<td>0.060 ± 0.003</td>
<td>3.38 ± 0.21</td>
</tr>
<tr>
<td></td>
<td>56.00</td>
<td>0.048 ± 0.00</td>
<td>2.71 ± 0.04</td>
<td>48.4 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>certified value,</td>
<td></td>
<td></td>
<td>49.5 % Ca</td>
</tr>
</tbody>
</table>
Table 4.13 continued

(iii), analysis of Ordinary Portland Cement for calcium

<table>
<thead>
<tr>
<th>method</th>
<th>stock, Absorbance</th>
<th>graph, %Ca found</th>
<th>accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>normal AAS:</td>
<td>125.77 0.320 ± 0.005</td>
<td>4.26 ± 0.10</td>
<td>34 ± 1</td>
</tr>
<tr>
<td></td>
<td>94.37 0.240 ± 0.005</td>
<td>3.15 ± 0.10</td>
<td>33 ± 1</td>
</tr>
<tr>
<td>normal AAS + La(III):</td>
<td>125.77 0.430 ± 0.010</td>
<td>5.71 ± 0.11</td>
<td>45.4 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>94.37 0.320 ± 0.005</td>
<td>4.24 ± 0.04</td>
<td>45.0 ± 0.5</td>
</tr>
<tr>
<td>manifold:</td>
<td>62.89 0.052 ± 0.005</td>
<td>3.23 ± 0.11</td>
<td>51 ± 2</td>
</tr>
<tr>
<td>t 39 μl;</td>
<td>47.06 0.043 ± 0.003</td>
<td>2.59 ± 0.25</td>
<td>55 ± 5</td>
</tr>
<tr>
<td>t t 50 μl.</td>
<td>74.93 0.059 ± 0.003</td>
<td>3.32 ± 0.21</td>
<td>44 ± 3</td>
</tr>
<tr>
<td></td>
<td>131.40 0.103 ± 0.007</td>
<td>5.77 ± 0.43</td>
<td>44 ± 3</td>
</tr>
<tr>
<td>certified value,</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[
\text{accuracy} = \frac{(\% \text{Ca})_{\text{found}} - (\% \text{Ca})_{\text{certified}}}{(\% \text{Ca})_{\text{certified}}} \times 100
\]

4.5.5. Discussion

The calcium contents of the samples of White Portland cement and Ordinary Portland cement, as obtained with the use of the developed in-line precipitation-dissolution procedure and by conventional aspiration of the samples after the addition of lanthanum chloride, were not significantly different from the suppliers' certified values. The two methods could offer similar accuracy of less than 5% except the result for calcium in Ordinary Portland Cement. This result, obtained from the manifold that incorporated the reaction coil and the filter membrane, was positively biased to an error of 19%. The reduced mixing of the reactants in this
manifold most likely permitted unreacted calcium ions to be adsorbed on concomitant gelatinous precipitates such as iron hydroxide. Such precipitates would be additionally retained on the filter and with inadequate wash times, would give a positive bias for calcium when eluted by the acid stream. The precision of the signals obtained from the precipitation-dissolution method was inconsistent at 2-11% RSD becoming better as the absorbance peak height increased (see Table 4.12). In summary, the studies in this chapter show that the analytical performance of on-line precipitations in FAAS could be improved as follows:

(a), an improvement in precision could be realised if the sensitivity is improved. This should be effected by increasing the precipitate yield as well as dissolving the precipitates at the pumping flow rates close to the nebuliser optimum uptake rate. The use of packed beds rather than reaction coil plus membrane filters would permit high dissolution flow rates (≥ 2 ml min⁻¹) without leaks in the manifold;

(b), an improvement in sensitivity over conventional nebulisation could be achieved by the preconcentration of samples from a large volume of the dilute solutions; and

(c), the linear range could be improved with the design of more efficient mixing and filtration devices. If a circulation loop is used as a reactor in the manifold, it should permit homogeneous mixing at all flow rate variations. This would increase the extent of reaction. The packed bed fitted with a membrane of finer pore (about 0.2 μm pore-size) could then be used to gather more precipitate fines.

4.5.6. Conclusions

The application of the designed manifold to determine calcium in samples of Portland cement offered an accuracy of 5% on the average.

The developed precipitation-dissolution method has the advantages of FIA such as using a limited sample volume in a contamination-free environment as well as the potential of sensitivity enhancement through the preconcentration of calcium from a large volume of solution.
REFERENCES


CHAPTER FIVE

ON-LINE PRECIPITATION FOR PRECONCENTRATION AND APPLICATIONS OF A CLOSED-LOOP MIXER IN FLOW INJECTION-FLAME ATOMIC ABSORPTION SPECTROMETRY

5.1. INTRODUCTION

Flame atomic absorption spectrometry (FAAS) is a technique widely used for the determination of trace concentrations of (mg l\(^{-1}\)) elements. However, the technique is not considered suitable for the direct determination of ultra-trace concentrations (\(\mu\)g l\(^{-1}\)) of analytes except for the vapour/hydride forming elements such as mercury, arsenic and selenium. This is because FAAS suffers from low absolute power of detection as well as large sample consumption.\(^{1,2}\) Critical views on these trends in analytical chemistry, as presented by prominent spectroscopists from both academia and industry, such as Hieftje, Slavin, Tolg and Townshend, consider electrothermal atomisation (ETAAS) to be a hundred to a thousand times superior to FAAS in terms of power of detection. Therefore, ETAAS is appropriate for ultra-trace determination of metallic elements.\(^{3-6}\) Electrothermal atomisation, however, suffers from severe matrix interferences and background absorption as well as extended analysis cycle time. A typical cycle time for ETAAS could be three or more minutes, whilst an FAAS measurement typically could be made in less than thirty seconds.\(^{7}\) Solutions to the problems of ETAAS are offered by the use of matrix modifiers, the L'vov platform and Zeeman background correction.\(^{8}\) It is also advantageous to have controlled and stable heating of the atomiser. All of these features make the technique of ETAAS complex in terms of instrumentation. This results in increased costs and a higher degree of operator expertise compared with using FAAS. The precision of 5 - 10% RSD for ETAAS\(^9\) is an additional demerit when compared to 0.5 - 1% RSD for FAAS.

There are techniques which have been applied to reduce the relatively large sample consumption as well as to improve the sensitivity of FAAS such as:

(a) discrete nebulisation technique; in which the sample consumption of normally 1 to 2 ml was reduced by the injection of 10 - 100 \(\mu\)l of liquids (of similar sample volumes as used in ETAAS);\(^{1,10,11}\)
(b), the flame gases and vapours are retarded by a slotted-tube atom "trap" placed in the flame so as to increase the residence time of atoms in the light path;12-14 and

(c), micro-amounts (5 to 40 µl) of the samples were either electrically heated on a wire loop to remove the solvent and then vaporised directly in the flame15 or vaporised by focussed infrared radiation to overcome nebulisation inefficiencies.16 Both methods were applied to the determination of more volatile elements such as cadmium and lead.

These techniques improve the detection limits of FAAS to µg l\(^{-1}\) values but not for the analytes with interfering matrix components without adequate sample pretreatment. Current developments in flow injection atomic absorption spectrometry (FI-AAS) are directed towards the development of sample pretreatment procedures (analyte isolation with simultaneous preconcentration) that are contamination-free. Sample consumption (as sample volume) in these procedures could be much reduced, in comparison with conventional FAAS, to unit microliters if required.17,18 Thus on-line ion-exchange, liquid-liquid extraction, precipitation and electrodeposition methods are being developed for FI-AAS. At present, these methods are applied to offer similar sensitivity with reduced analysis time compared with ETAAS. Reports on such developments have been presented in section 1.3.3.

For example, the preconcentration of lead from tap water by the precipitation reaction with ammonia was reported by Martinez-Jimenez and coworkers.19 The precipitates were retained on a stainless steel filter and subsequently dissolved with nitric acid for determination in FAAS. The degree of enrichment increased as the feed volume of the sample increased such that a detection limit of 1 µg l\(^{-1}\) was achieved for a 250 ml-sample volume. The precision was 3.6% RSD with a throughput of 1 h\(^{-1}\).

Continuous precipitation flotation with recycle, an off-line precipitation technique, is used in inorganic analysis for the preconcentration of ultratrace concentrations of metal ions. This technique is known to offer very high enrichment factors. Thus a hundred litre water sample that contained cadmium at ng l\(^{-1}\) concentrations, was concentrated to offer an enrichment factor of two thousand.20 However, the period for the sample run was 2.5 hours. The period covered the precipitation reaction, flotation, extraction of the cadmium from precipitates and subsequent solvent removal by evaporation. The drawbacks of off-line determinations using precipitation reactions include: (a), inconsistent recoveries, due to the multi-stage manipulative procedures; (b), low sample throughput, due to requirements that the analyte be concentrated to major concentrations so as to reduce errors; and (c),
exposure to contamination from the surroundings.

This chapter reports on the design of a merging stream manifold that incorporated a confluence mixer and a minicolumn of polystyrene granules prior to a PTFE membrane filter, for the precipitation of basic calcium oxalate. The manifold was applied for:

(a), the preconcentration and determination of calcium in synthetic rock solutions; and

(b), the determination of solubility product of calcium oxalate.

For the latter application, the confluence mixer was replaced with a closed-loop mixer. The use of a similar manifold with a closed-loop mixer for the dilution of a stock solution for calibration purposes was also investigated.

5.2. APPARATUS AND REAGENTS

The merging-stream manifolds used in the experiments were constructed from PTFE tubing of internal diameter 0.58 mm. The peristaltic pump was a Gilson Minipuls-2 fitted with PVC tubings of 0.4 mm internal diameter for the water carrier and reagent streams and 2.05 mm internal diameter for the acid stream. The filter unit was a minicolumn of polystyrene granules, 0.5 mm diameter, packed into a PTFE tube (5 cm long and 3 mm diameter) together with a PTFE membrane filter (0.2 μm pore-size and 5 mm diameter). The unit provided a graded collection of precipitates such that excessive pressure which could cause leaks in the manifold was removed. The pulse suppressors used in the water carrier/wash and reagent streams were removed which improved the mixing of the reactants for the precipitation reaction. The air compensation inlet was through a PTFE tube (5 cm long and 0.58 mm internal diameter) connected to an omnifit T-piece.

All absorbances were measured with a Baird-Atomic, Model A3400, spectrometer connected to a Philips AR55 chart recorder.

All glass ware was soaked in 30% (v/v) nitric acid after cleaning and rinsed with reagent water when needed.

All solutions used in the experiments were prepared by the dilution of stock 1000 mg l⁻¹ solutions (BDH SpectrosoL grade) except for the ammonia- ammonium oxalate reagent which was prepared from BDH AnalaR grade compounds. Reagent
grade water, produced by a LiquiPure RG system (reverse osmosis followed by ion exchange), was used for dilutions and as the carrier/wash streams.

5.3. PRECONCENTRATION AND DETERMINATION OF CALCIUM IN SYNTHETIC ROCK SOLUTIONS

The results of the optimum conditions for the chemical and flow variables offered in chapter four of this report (see section 4.4), were considered for the construction of the manifold shown in Fig. 5.1. The precipitation of calcium oxalate in the cold required a contact time of 3 minutes or more for an appreciable precipitation as well as careful control of the pH of the reacting mixture. Therefore the water carrier and the ammonia-ammonium oxalate stream were pumped at low flow rates of less than 1 ml min\(^{-1}\). This was used to increase the residence time of the reaction mixture in the manifold. The pH of the 0.05 M ammonia with 50 mg l\(^{-1}\) ammonium oxalate monohydrate was 10 and above for the selective precipitation of calcium from aluminium interferent.

The manifold was applied for the preconcentration of calcium and the sample was pumped to merge with the reagent. However, an injection valve, a 4-way rotary valve (Rheodyne, model 5041), was fitted after the pump at 26 cm from the Y-piece for the injection of small sample volumes when required.

5.3.1. Procedures and results

Preliminary experiment — The effect of pumping flow rate on the absorbance of calcium was used to check the efficiency of the filter unit (minicolumn of polystyrene granules with 0.2 μm pore size, PTFE membrane filter fitted in its outlet) in the manifold in Fig. 5.1. The spectrometer was operated with the settings for the determination of calcium at maximum sensitivity in air-acetylene flame. The nebuliser liquid uptake rate with these settings was 8 ml min\(^{-1}\). The effect of pumping flow rate on the precipitation-dissolution of 50 μl injections of 10 mg l\(^{-1}\) calcium was studied. The cycle time for the injection, precipitation and dissolution sequences was 5 minutes (see the procedure of section 4.4.3(i)). The results are shown in Fig. 5.2.
Fig. 5.1. Merging streams manifold for the preconcentration of calcium using precipitation, filtration and subsequent stream dissolution with 5% HCl. C, water wash; R, 0.05 M ammonia with 50 mg l\(^{-1}\) ammonium oxalate monohydrate; S, sample inlet; Pc, precoil; Ps, pulse damper; Y, confluence mixer; m, minicolumn of polystyrene granules; f, PTFE membrane (0.2 \(\mu\)m pore-size, 5 mm f.d.); v1, 4-way rotary valve as stream selector; v2 and v3, stream-switching valves; a, air compensation inlet; T, PTFE tee-connector; length of tube between Y and m was 2 cm, m and f was 5 cm, and between T and AAS was 3 cm.

In-house packing of membrane filter:
1, end-connector;
2, O-ring (5mm bore, 1 mm thick);
3, coupling-connector;
4, teflon frit (25 \(\mu\)m pore-size, 5 mm diameter, 1 mm thick);
5, PTFE membrane (0.2 \(\mu\)m pore-size, 5 mm diameter);
6, Teflon truncated cone (4 mm bore); and 7, omnifit tee.
Fig. 5.1. Operation of the valves in the merging-stream manifold for the preconcentration of calcium: (I), sample stream selection; and (II), acid stream selection.
The optimum pumping flow rates used to operate the manifold for further experiments, were 0.37, 0.28 and 1.4 ml min$^{-1}$ for the water carrier, reagent and the acid streams, respectively. These values were deduced from Fig. 5.2.

**Preconcentration**  The manifold shown in Fig. 5.1 was used. Three standard solutions of calcium with concentrations 200, 20 and 2 μg l$^{-1}$ were used, in turn, as the test solution which was pumped from a burette. The precipitation-dissolution cycle started with water and reagent pumped through the acid-washed filter unit to the nebuliser to establish the base line. Then, 5% HCl was pumped at 5 minutes intervals for the blank absorbances. Three replicate blank absorbances were recorded.
The operation sequence for the pumped sample with reagent followed by dissolution of the precipitates was:

- a fixed volume of a test solution and the reagent was pumped for the precipitation stage. Then, water and reagent were pumped for a wash period of 2 minutes. Finally, the acid was pumped to dissolve the precipitate and the absorbance peak was recorded at 120 s cm$^{-1}$.

The cycle was replicated three times and the procedure was repeated for seven other volumes (of increasing magnitude) of the same test solution. The experimental run for each test solution finished with repeat blank determinations before close down.

The plot of the results is shown in Fig. 5.3.

![Graph](image)

**Fig. 5.3.** Effect of sample volume on the preconcentration of calcium in the merging-stream manifold for precipitation-dissolution of basic calcium oxalate. The precipitation flow rate was 0.65 ml min$^{-1}$ and dissolution flow rate was 1.4 ml min$^{-1}$ for:

- (△), 2 μg l$^{-1}$ Ca;
- (●), 20 μg l$^{-1}$ Ca; and
- (○), 200 μg l$^{-1}$ Ca.

* Absorbance for the conventional aspiration of 200 μg l$^{-1}$ Ca; and the nebuliser liquid uptake was 8 ml min$^{-1}$.

**Determination of calcium in synthetic rock solutions** — In Fig. 5.3, the graph of the absorbance of calcium against the pumped volume of sample was linear, within a certain volume range, for a given concentration. The range of
volumes for linearity decreased as the concentration of the test solution increased. Therefore, it was necessary to establish the linear ranges of the normal calibration graphs for calcium when different volumes were used as the sample volume in the manifold shown in Fig. 5.1.

Normal working curves were prepared with the standard solutions made up for the different sample volumes: (a), 0.4 - 4 mg l\(^{-1}\) Ca, for 140 µl; (b), 0.001 - 0.015 mg l\(^{-1}\) Ca, for 5 ml and 10 ml. The operation sequence for the precipitation-dissolution cycle was similar to that described for preconcentration. The 5 ml and 10 ml sample volumes were pumped but the 140 µl volumes were injected at a tube length of 26 cm from the confluence mixer. The standard solutions were aspirated conventionally for comparison. The characteristics of the normal working curves are presented in Table 5.1. They were deduced from the results shown in Fig. 5.4.

### Table 5.1. Characteristics of normal working curves for the precipitation manifold compared with conventional aspiration

<table>
<thead>
<tr>
<th>parameter</th>
<th>normal AAS</th>
<th>precipitation manifold</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear range, mg l(^{-1})</td>
<td>140 µl</td>
<td>5 ml</td>
</tr>
<tr>
<td>characteristic concentration, mg l(^{-1})</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>d.l., (3 s.d.), mg l(^{-1})</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>enrichment factor*</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>throughput, h(^{-1})</td>
<td>-</td>
<td>12</td>
</tr>
</tbody>
</table>

* enrichment factor is the ratio of the slopes of regression equation for each normal curve compared to normal AAS.

<table>
<thead>
<tr>
<th>regression equations</th>
<th>corr. coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>normal AAS</td>
<td></td>
</tr>
<tr>
<td>manifold: 140 µl;</td>
<td>Abs = 0.005 + 0.0557 × Conc</td>
</tr>
<tr>
<td>5 ml;</td>
<td>Abs = 0.021 + 0.0578 × Conc</td>
</tr>
<tr>
<td>10 ml</td>
<td>Abs = 0.018 + 6.200 × Conc</td>
</tr>
</tbody>
</table>
Normal working curves for calcium using the manifold shown in Fig. 5.1 for preconcentration. Flow rates for precipitation and dissolution were 0.65 and 1.40 ml min\(^{-1}\); sample volume for each curve was: \((\ast)\), 10.00 ml; \((\triangle)\), 5.00 ml; and \((\ast)\), 140 \(\mu\)l. 

\((o-o)\), normal working curve for calcium using conventional aspiration with the nebuliser liquid uptake rate as 8 ml min\(^{-1}\).
The synthetic rock solutions were made up with constituent ion concentrations as shown in Table 5.2. These ion concentrations were identical to the certified values of the corresponding standard reference materials\(^{21}\). The calibration graph for the 140 \( \mu l \) sample volume afforded the best linear range for the precipitation-dissolution of calcium in the manifold shown in Fig. 5.1 (see Table 5.1). Therefore, 140 \( \mu l \) injections were made for the synthetic rock samples. In addition, the synthetic rock solutions were aspirated conventionally for comparison. The results are shown in Table 5.3.

### Table 5.2. Solution make-up for the synthetic rock samples

<table>
<thead>
<tr>
<th>* rock</th>
<th>concentration of ions in solution, mg 1(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca</td>
</tr>
<tr>
<td>glass sand</td>
<td>1</td>
</tr>
<tr>
<td>(SRM 1413)</td>
<td></td>
</tr>
<tr>
<td>glass soda lime sheet</td>
<td>9</td>
</tr>
<tr>
<td>(SRM 1831)</td>
<td></td>
</tr>
<tr>
<td>phosphate rock western</td>
<td>35</td>
</tr>
<tr>
<td>(SRM 694)</td>
<td></td>
</tr>
<tr>
<td>iron ore Sileby</td>
<td>1</td>
</tr>
<tr>
<td>(SRM 27f)</td>
<td></td>
</tr>
<tr>
<td>manganese ore</td>
<td>1</td>
</tr>
<tr>
<td>(SRM 25d)</td>
<td></td>
</tr>
<tr>
<td>chrome refractory</td>
<td>1</td>
</tr>
<tr>
<td>(SRM 103a)</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.3. Absorbance of the solutions of calcium and results for the determination of calcium in synthetic solutions of rock samples

<table>
<thead>
<tr>
<th>solution</th>
<th>mg l⁻¹</th>
<th>normal AAS</th>
<th>140 µl injection</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>0.40</td>
<td>0.030 ± 0</td>
<td>0.038 ± 0.004</td>
</tr>
<tr>
<td>2</td>
<td>1.00</td>
<td>-</td>
<td>0.087 ± 0.006</td>
</tr>
<tr>
<td>3</td>
<td>2.00</td>
<td>0.120 ± 0.002</td>
<td>0.134 ± 0.008</td>
</tr>
<tr>
<td>glass sand</td>
<td>0</td>
<td>0</td>
<td>0.078 ± 0.007</td>
</tr>
<tr>
<td>glass soda, (D.F. 10)</td>
<td>0.025</td>
<td>± 0</td>
<td>0.077 ± 0.003</td>
</tr>
<tr>
<td>phosphate rock, (D.F. 25)</td>
<td>0.185</td>
<td>± 0.005</td>
<td>0.100 ± 0.01</td>
</tr>
<tr>
<td>iron ore</td>
<td>0.065</td>
<td>± 0.005 *</td>
<td>0</td>
</tr>
<tr>
<td>manganese ore</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>chrome refractory</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

regression equation:

\[ A = 0.005 + 0.0557 \, C \]  
\[ A = 0.021 + 0.0578 \, C \]

corr. coeff.: 0.998 0.992

linear range: 0 - 4.00 mg l⁻¹ 0 - 2.5 mg l⁻¹

<table>
<thead>
<tr>
<th>mg l⁻¹ Ca, found</th>
<th>mg l⁻¹ Ca certified</th>
</tr>
</thead>
<tbody>
<tr>
<td>normal AAS</td>
<td>140 µl injection</td>
</tr>
<tr>
<td>glass sand</td>
<td>0</td>
</tr>
<tr>
<td>glass soda</td>
<td>3.6</td>
</tr>
<tr>
<td>phosphate</td>
<td>32.4</td>
</tr>
<tr>
<td>iron ore</td>
<td>1.1 *</td>
</tr>
<tr>
<td>manganese ore</td>
<td>0</td>
</tr>
<tr>
<td>chrome refractory</td>
<td>0</td>
</tr>
</tbody>
</table>

D.F., dilution factor

* iron ore showed absorbance for calcium, ONLY in the presence of excess citric acid.

A, absorbance; C, concentration, mg l⁻¹; and corr. coeff., correlation coefficient.
5.3.2. Discussion

The precipitation of calcium oxalate with the use of the manifold in Fig. 5.1 was applied to concentrate \( \mu g \cdot l^{-1} \) concentrations of calcium without the requirement of a carrier (see Fig. 5.3). The degree of enrichment increased as the sample volume increased. The increasing enrichment was eventually limited by the filtration capacity of the filter unit. At this stage in the preconcentration, the plot of absorbance versus concentration which had been linear curved towards the concentration axis. It could be adduced that the filter unit was losing some of the precipitates because the dissolution procedure with a stream of 5\% HCl showed sharp FI- absorbance profiles. Otherwise, the absorbance profile would have been a plateau if the strength of 5\% HCl was the limitation. Consequently, the manifold offered a precision of 4\% RSD or less in the linear portion of the absorbance versus concentration graphs and the precision could worsen to 10\% for curved portions of the graphs where the filter capacity was exceeded. The characteristics of the calibration graphs varied with the sample volume (see Fig 5.4 and Table 5.1) such that the linear range for the determination of calcium narrowed and shifted to lower concentrations as the sample volume increased. The sensitivity was, however, improved that a 10 ml sampling at a throughput of 2 h\(^{-1}\) offered an enrichment factor of 880 (the enrichment factors were evaluated by comparison of the sensitivities with those obtained by conventional aspiration). A demerit of the designed manifold (see Fig. 5.1), is the requirement of low pumping flow rate for increased precipitation which resulted in a low sample throughput. A further observation from the experiments was the need for the reagents to be of high purity (at best 100\% analyte-free) for the determinations to be reliable. This would minimise errors in the analysis of solutions with concentrations close to the blank.

The separation of calcium from a matrix with two or more interferents, such as aluminium, phosphate and silicon, is demonstrated in the analysis of synthetic rock solutions (see Table 5.3). The results for "glass sand", "glass soda lime sheet" and "phosphate rock western" were accurate to within 2\% error with the use of manifold in Fig. 5.1. These samples were difficult to analyse for calcium with conventional aspiration. The reasons were that the absorbance of "glass sand" was negligible and the absorbance of "glass soda lime sheet" as well as "phosphate rock western" were depressed.

The operation of manifold 5.1, however, failed to give any result for the "iron ore", "manganese ore" and "chrome refractory". It was observed that the cations in these
samples formed coloured precipitates with the ammonia-ammonium oxalate reagent. The calcium and aluminium ions in the samples were, most likely, not precipitated or jointly precipitated. This is because there was neither an effluent nor a 5% HCl-dissolution absorbance for calcium. The absorbance of calcium would have been depressed by the aluminium as the two ions were jointly present in the sample bolus. The addition of masking agents such as EDTA and citric acid, in controlled and then excess amounts, to either the samples or the reagent (as is the practice in the classical precipitation methods\textsuperscript{22-24}) offered no absorbance for calcium with the precipitation procedure. Therefore, it was concluded that the slow kinetics of calcium oxalate precipitation permitted the rapid depletion of the reagent, ammonia, by the interfering metallic ions. This caused the pH of the reaction mixture to decrease (below pH 10) and, hence, calcium/oxalate precipitation could not occur.

### 5.3.3. Conclusions

Preconcentration of $\mu$g l\(^{-1}\) concentrations of calcium could be effected with the manifold in Fig. 5.1.

The devised procedure offered high concentration factors (about 800) when a large volume of a sample solution of trace calcium was pumped. However, the precipitation cycle time was long (about 30 minutes for an enrichment of 800). The devised procedure was very sensitive to trace concentrations of calcium so that the determination of calcium in the solutions with concentrations close to the blank ($\leq 2 \mu$g l\(^{-1}\)) was prone to error.

The selective precipitation of calcium from anionic interferents (phosphate and silicon) and amphoteric interferent (aluminium) could be effected with 2% error in the determination of calcium. Cations that would readily form precipitates with ammonia must be absent otherwise calcium would not precipitate as the oxalate with the ammonia-ammonium oxalate reagent at room temperature.

### 5.4. DETERMINATION OF THE SOLUBILITY PRODUCT OF CALCIUM OXALATE

The precipitation of calcium as the oxalate with use of ammonia-ammonium oxalate reagent (pH $\geq10$) occurred at room temperature though the reaction was of slow kinetics (see section 4.4). The precipitation of calcium oxalate caused the complete
removal of aluminium, phosphate and silicon interferences in the determination of calcium in real samples such as cement (see section 4.5). The application of calcium/oxalate procedure to the determination of calcium in synthetic rock solutions, however, showed some difficulties. There was chemical interference from relatively large concentrations of concomitant heavy cations (see Tables 5.2 and 5.3). In this case, it is most likely that the calcium/oxalate reaction failed to occur on thermodynamic considerations. Therefore, it was necessary to ascertain the nature of calcium/oxalate precipitation at ambient temperature. For this purpose, a manifold with a closed-loop precipitator was devised for the determination of the solubility product of calcium oxalate.

5.4.1. Manifold design and operation

Manifold design — The manifold in Fig. 5.5 was devised such that the circulatory flows of liquid within a closed-loop were used to effect the mixing of the

![Diagram](image)

**Fig. 5.5.** Manifold with closed loop for the determination of the solubility product of calcium oxalate by precipitation, filtration and subsequent stream dissolution with 5 % HCl.

C, water wash; R, 0.05 M ammonia with 50 mg l\(^{-1}\) ammonium oxalate reagent; S, sample inlet; Pc, precoil; Ps, pulse damper; L, closed-loop; m, minicolumn of polystyrene granules; f, packed PTFE membrane (0.2 µm pore-size, 5 mm f.d.); v1, two nested 4-way rotary valves as stream selector; v2 and v3, stream-switching valves; a, air compensation inlet; and T, PTFE tee-connector. Length of tube between nested valves and m was 28 cm, and between T and AAS was 8 cm.
reactants. This is expected to produce a complete mix of the reactants more than the flow mechanism afforded previously, with a confluence mixer of the manifold in Fig. 5.1. The peristaltic pump was connected "end on" to two nested 4-way rotary valves (Rheodyne, model 5041) to cause a circulatory flow of the liquid within the closed-loop as depicted in Fig. 5.6. The effect of the number of circulatory flows on the precipitation and hence on the absorbance of 10 mg l\textsuperscript{-1} Ca was studied using the manifold.
Manifold operation. In the first operation, the pump roller head control was fixed at a setting and the time for one circular liquid flow in Fig. 5.6.1(III) was determined thus:

(a) the 0.05 M ammonia with 50 mg l\(^{-1}\) AOM was pumped through the manifold with the two valves set at "inject" positions as shown in Fig. 5.6.1(I);
(b) with both valves set at "load" positions, the sample loop was filled with air (see Fig. 5.6.1(II));
(c) the valve connected to the pump was set on "inject" position for the air segment to move round the closed-loop; and
(d) the time for the consecutive passage of the leading air/liquid boundary into the second valve was noted.

The average of five replicate times was used as the time of one circular liquid flow in the closed-loop. Then, as the operation of the nested valves was returned to the state in Fig. 5.6.1(I), the switching valve (v2) in manifold 5.5 was set such that the air plug emptied to waste whilst the reagent flowed through the manifold.

In the second operation, the sequence of switching the nested valves was carried out for the sample loop now filled with a solution of 10 mg l\(^{-1}\) Ca. After one circulatory flow of liquid in the closed loop, the reaction mixture was pumped to the filter unit which retained the precipitates. Whilst the sequence of operation of the nested valves was being repeated for two circulations of an identical reaction mixture, water was drawn by nebuliser suction to wash the precipitates. The wash period was 5 seconds before a 5% HCl solution was pumped to dissolve the precipitates. The absorbance was recorded at 120 s cm\(^{-1}\). The absorbances of identical reaction mixtures, with three and more circulations used for mixing, were similarly recorded.

The entire procedure; for the determination of the time for one circulatory liquid flow in the closed-loop and the precipitation of calcium followed with dissolution, was replicated at different settings of the pump roller head control. The results are shown in Table 5.4.

The results in Table 5.4 show that a single circulatory flow of liquid in the closed-loop could cause sufficient precipitation as produced by two or more circulations. This is evidenced in the absorbance for 10 mg l\(^{-1}\) calcium which, with two or more circulatory mixes of the reaction mixture, was not significantly increased to offer an extra advantage. Also, the absorbance of calcium decreased as the pumping flow rates increased. A possible explanation for this curious trend could be that fine precipitates were being lost at the filter unit such that the loss
Table 5.4. Effect of the number of circulatory liquid flows in a closed-loop on the precipitation and absorbance of 10 mg l⁻¹ calcium in manifold 5.5.

<table>
<thead>
<tr>
<th>flow rate, ml min⁻¹</th>
<th>time for precipitation; elution</th>
<th>time for circular mix</th>
<th>Absorbance for 10 mg l⁻¹ Ca with circular liquid flows of:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>0.24</td>
<td>0.56</td>
<td>160 s</td>
<td>9 min</td>
</tr>
<tr>
<td>0.36</td>
<td>0.80</td>
<td>80 s</td>
<td>8 min</td>
</tr>
<tr>
<td>0.58</td>
<td>1.60</td>
<td>40 s</td>
<td>4 min</td>
</tr>
<tr>
<td>1.40</td>
<td>2.80</td>
<td>20 s</td>
<td>2 min</td>
</tr>
<tr>
<td>2.10</td>
<td>4.80</td>
<td>12 s</td>
<td>1.5 min</td>
</tr>
<tr>
<td>2.80</td>
<td>6.00</td>
<td>9 s</td>
<td>1 min</td>
</tr>
</tbody>
</table>

* A precipitation-dissolution cycle for which the stated times were the minimum applied with 1 circulatory mixing of the reactants in a closed-loop.

increased as the pumping flow rate increased. If the precipitate fines make a significant contribution to the absorbance of the reaction effluents, then the determination of the solubility product of calcium oxalate would predictably afford better results in the low pumping flow rate region.

5.4.2. Basis of the method

The precipitation of calcium oxalate from a solution containing excess of either of its constituent ions would normally occur by the common ion effect. In which case, the concentration of the ions in equilibrium with the solid would obey the solubility product expression.

For the reaction: \( \text{CaC}_2\text{O}_4(s) \leftrightarrow \text{Ca}^{2+}(aq) + \text{C}_2\text{O}_4^{2-}(aq) \) \hspace{1cm} 5.1

\[ K_{s0} = \{\text{Ca}^{2+}\} \{\text{C}_2\text{O}_4^{2-}\} \] \hspace{1cm} 5.2

where, \( K_{s0} \) is the solubility product at zero ionic strength; and \( \{ \} \) are the activities of the ions in the saturated solution.
In dilute solutions the activity of an ion is equal to its molar concentration,
\[ K_{s0} = [Ca^{2+}] [C_2O_4^{2-}] \] ...................... 5.3

Calculations of solubility product of calcium oxalate:
operation or manifold 5.5

Let \( V \) be the volume (μl) of the closed-loop in Fig. 5.6.(III);
\( v \) be the volume (μl) of the closed-loop in Fig. 5.6.(II);

where, \((V-v)\) is the volume (μl) of the sample loop.

Also,
let \( C_{0,ca} \) be the molar concentration (mol l\(^{-1}\)) of calcium ions in the test solution;
\( C_{0,ox} \) be the concentration (mol l\(^{-1}\)) of the oxalate ions in the buffer; and
\( \phi \) be the precipitation efficiency;

where, \( \phi \) is the fraction of the concentration of calcium ions precipitated (that is, \( \phi \) is 1 minus the ratio of the absorbance of calcium in precipitation effluents to the absorbance of calcium in water streams without the reagent).

The dilution of the solutions in the closed-loop in Fig. 5.6.(III) gives
\[ (V-v)/V \cdot C_{0,ca} \] as the initial concentration of calcium ions; and
\[ v/V \cdot C_{0,ox} \] as the initial concentration of the oxalate reagent.

\[ (V-v)/V \cdot \phi \cdot C_{0,ca} \] is the concentration of calcium ions in precipitates.

From equation 5.1,
\[ (V-v)/V \cdot \phi \cdot C_{0,ca} \] would also be the concentration of oxalate ions in precipitates;
that is,
\[ \{(V-v)/V \cdot C_{0,ca}\} - [(V-v)/V \cdot \phi \cdot C_{0,ca}] \] is the equilibrium concentration for calcium ions; and
\[ \{v/V \cdot C_{0,ox}\} - [(V-v)/V \cdot \phi \cdot C_{0,ca}] \] is the equilibrium concentration for oxalate ions.

The substitution of these concentration values into the solubility product expression in equation 5.3 gives,
\[ K_{s0} = \{(V-v)/V \cdot C_{0,ca}\} - [(V-v)/V \cdot \phi \cdot C_{0,ca}] \]
\[ \cdot \{v/V \cdot C_{0,ox}\} - [(V-v)/V \cdot \phi \cdot C_{0,ca}] \] ...................... 5.4

However, \( K_{s0} \), as calculated in equation 5.4, would provide the apparent solubility product for calcium oxalate if the manifold reaction has not attained equilibrium within the 5 minutes of the precipitation cycle.
5.4.3. Procedure and results

The manifold shown in Fig. 5.5 was used. The spectrometer was operated with the settings for the determination of calcium at maximum sensitivity. The nebuliser liquid uptake with the settings was 8.0 ml min⁻¹. The time (average of five replicates) for one circulatory flow of liquid in the closed-loop in Fig. 5.6.(II) was determined by timing the consecutive passage of the leading air/liquid boundary, into the valve connected the pump, at a fixed pumping flow rate of 0.24 ml min⁻¹. This time was 102 seconds. A similar determination for the closed loop in Fig. 5.6.(III) gave 160 seconds for one circulation. The product of flow rate and time gave the volumes of liquid that would fill the closed loops as 408 µl and 640 µl, respectively. Therefore the difference between these values gave the volume of the sample loop, as 232 µl.

Injections of 232 µl of 10 mg l⁻¹ calcium were made and mixed with 408 µl of 0.05 M NH₃ with 50 mg l⁻¹ AOM in the closed-loop of Fig. 5.6.(III). The mixture was circulated for 5 minutes and then pumped through the filter unit to the nebuliser. The absorbance of the effluents was recorded. The precipitates were dissolved with a stream of 5 % HCl as described in the operation of the manifold in section 5.4.1. The precipitation-dissolution sequence was replicated three times and the procedure was carried out at different pump settings that offered precipitation flow rates from 0.24 to 2.8 ml min⁻¹ with corresponding dissolution flows of 0.56 to 6 ml min⁻¹.

The experiment was carried out for the water stream without reagent, so as to record the absorbances for 10 mg l⁻¹ calcium without the precipitation reaction. The results are shown in Table 5.5. The calculation of the solubility product is as explained previously (see section 5.4.2).

5.4.4. Discussion

The apparent solubility product for calcium oxalate at ambient temperature was found to be \((8 \pm 1) \times 10^{-9}\) mol² l⁻² (see Table 5.5). This value is roughly a factor of four higher than the reported solubility product for calcium oxalate \((K_{sp} \text{ at } 25^\circ \text{C}, 2 \times 10^{-9}\) mol² l⁻²). The reason for the high value could be one or both of the following: (a), the calculated solubility product was obtained for a five minutes mixing. Hence, the reaction mixtures had not attained equilibrium. The values, however, show these mixtures as not far removed from equilibrium; and (b), it is
Table 5.5. Results for the absorbance of 10 mg l⁻¹ calcium solution in manifold of Fig. 5.5 and calculation of the solubility product of calcium oxalate

(i), Absorbance at different pumping flow rates:

<table>
<thead>
<tr>
<th>flow rate, ml min⁻¹</th>
<th>Absorbance for a 10 mg l⁻¹ Ca solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>no reagent</td>
</tr>
<tr>
<td>ppted</td>
<td>dissolution</td>
</tr>
<tr>
<td>0.24</td>
<td>0.56</td>
</tr>
<tr>
<td>0.36</td>
<td>0.80</td>
</tr>
<tr>
<td>0.58</td>
<td>1.60</td>
</tr>
<tr>
<td>1.40</td>
<td>2.80</td>
</tr>
<tr>
<td>2.10</td>
<td>4.80</td>
</tr>
<tr>
<td>2.80</td>
<td>6.00</td>
</tr>
</tbody>
</table>

(ii), calculation data for solubility product (Kₘ₀), of calcium oxalate:

<table>
<thead>
<tr>
<th>flow, ml min⁻¹</th>
<th>% Ca ppted</th>
<th>CaC₂O₄ (mol l⁻¹ x 10⁵)</th>
<th>[Ca ++] (mol l⁻¹ x 10⁵)</th>
<th>[(COO)₂⁻] (mol² l⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.24</td>
<td>56.25</td>
<td>5.098</td>
<td>3.965</td>
<td>17.41</td>
</tr>
<tr>
<td>0.36</td>
<td>52.63</td>
<td>4.770</td>
<td>4.293</td>
<td>17.73</td>
</tr>
<tr>
<td>0.58</td>
<td>52.63</td>
<td>4.770</td>
<td>4.293</td>
<td>17.73</td>
</tr>
<tr>
<td>1.40</td>
<td>57.89</td>
<td>5.248</td>
<td>3.816</td>
<td>17.26</td>
</tr>
<tr>
<td>2.10</td>
<td>45.87</td>
<td>4.157</td>
<td>4.905</td>
<td>18.35</td>
</tr>
<tr>
<td>2.80</td>
<td>46.77</td>
<td>4.238</td>
<td>4.824</td>
<td>18.27</td>
</tr>
</tbody>
</table>

† % Ca ppted = 100 (Abs no reagent - Abs effluent) / Abs no reagent.

* certified Kₘ₀ at 25 °C, 2.0 x 10⁻⁹ mol² dm⁻⁶.

In the experiment, 232 μl of 10 mg l⁻¹ (0.25 mM) Ca was mixed with 408 μl of 0.05 M NH₃ with 50 mg l⁻¹ (0.352 mM) ammonium oxalate monohydrate in a closed-loop.
possibile that the precipitate fines that passed through the filter caused a positive error in the absorbance of the calcium effluents which would give a low value of precipitation efficiency. This, in turn, would result in higher values for equilibrium concentration of the constituent ions than actually obtain in the reaction mixture. Hence the product of these concentrations for the solubility product would be high. Supporting evidence for the second reason is that precipitation efficiency, which should have remained constant with flow rate, decreased at a relatively high flow rate of above 2 ml min\(^{-1}\) (see Table 5.5(ii)).

The results for the absorbance trend of the dissolved precipitates (see Tables 5.4 and 5.5(i)) were consistent with the conclusions of the previous experiments in Chapter 4, namely that optimum performance in the manifold for the precipitation of calcium oxalate occurred when precipitation was carried out at pumping flow rates of less than 1 ml min\(^{-1}\). This is due to the slow kinetics of the precipitation reaction which required the use of low pumping flow rates to provide a longer residence time. This condition would be imperative for the manifold designs that used manifold dispersions as the major mixing mechanism. Such designs would have the demerit of low sample throughput and possibly incomplete interference removal as observed in the previous chapter (see Fig. 4.17). However, the incorporation of an agitated mixing mechanism such as the circulatory motion in a closed-loop in manifold 5.5, offered precipitation at high flow rates (see Tables 5.4 and 5.5(ii)). As a result, the contact time for the reactants could be reduced to one minute or less, without much change in the precipitation efficiency of calcium oxalate.

5.4.5. Conclusions

A manifold with the pump in a closed-loop is demonstrated as suitable for the determination of the solubility product of calcium oxalate.

The reactants were mixed by circulatory flow of the liquids that the precipitation of calcium oxalate was close to equilibrium within 5 minutes or less (at pumping flow rates of \(\geq 2\) ml min\(^{-1}\)).

5.5. APPLICATION OF A MANIFOLD WITH A CLOSED-LOOP MIXER FOR DILUTION AND CALIBRATION PURPOSES

The validity of efficient mixing afforded by the circulatory flow of liquids in a
closed-loop had been demonstrated in section 5.4, and it is further tested in this section. The closed-loop mixer is used to dilute a 10 mg l⁻¹ calcium solution to a negligible absorbance as recorded by the spectrometer. The results obtained are used to calculate the dilution factor afforded by the manifold.

5.5.1. Manifold design and operation

![Diagram of manifold design and operation]

Fig. 5.7. Manifold with closed-loop for the infinite dilution of calcium solution and single-standard normal calibration of Baird (Model A3400) spectrometer. C, water carrier; S, sample inlet; Pc, precoll; Ps, pulse damper; L, closed-loop mixer; and v1, two nested 4-way rotary valves. Tube length between nested valves and AAS was 30 cm.
The two nested 4-way rotary valves (Rheodyne, Model 5041) used in the previous section (see section 5.4.1) was incorporated into the manifold shown in Fig. 5.7. The peristaltic pump was connected "end on" to two nested 4-way rotary valves (Rheodyne, model 5041) to cause a circulatory flow of the liquid within the closed-loop as shown in the insert in Fig. 5.7. The injection volume for the sample loop and the volume for the closed-loop mixer had been determined previously to be 232 μl and 640 μl, respectively (see section 5.4.1).

5.5.2. Basis of the normal calibration procedure with a single standard

Operation of manifold 5.7.
Let

\[ V_L \]  be the volume of the closed-loop; and  
\[ v \]  be the volume of the solution injected at intervals which is automatically replaced with the diluent (the carrier stream).

The concentrations produced by the successive injections are given in Table 5.6.

Table 5.6. Theoretical concentrations generated by a finite number of successive injections and dilutions in the manifold with a closed loop mixer shown in Figure 5.7.

<table>
<thead>
<tr>
<th>injection</th>
<th>dilution</th>
<th>concentration of solution injected</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>[ C_0 = C_0 \cdot \left(\frac{V_L - v}{V_L}\right)^0 ]</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>[ C_1 = C_0 \cdot \left(\frac{V_L - v}{V_L}\right)^1 ]</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>[ C_2 = C_0 \cdot \left(\frac{V_L - v}{V_L}\right)^2 ]</td>
</tr>
<tr>
<td>(n+1)</td>
<td>n</td>
<td>[ C_n = C_0 \cdot \left(\frac{V_L - v}{V_L}\right)^n ]</td>
</tr>
</tbody>
</table>

\[ \left(\frac{V_L - v}{V_L}\right) \] is the reciprocal of the dilution factor.

In the first case, if it is assumed that there is a linear relation between absorbance and concentration, the conventional calibration curve is a plot of absorbance (A) versus concentration (C):

\[ A_n = k c_n \]

The successive dilutions carried out with a single standard solution in manifold 5.7
make concentration a function of the number of dilutions as shown in Equation 5.6. The substitution of Equation 5.6 into Equation 5.7 gives:

$$A_n = kC_0 \cdot \left[\frac{V_L - \nu}{V_L}\right]^n$$ ........................................ 5.8

Since $kC_0 \cdot \left[\frac{V_L - \nu}{V_L}\right]$ is a constant then, a plot of $A_n$ against $n$ would be exponential.

In the second case, for the $(n + 1)^{th}$ injection (that is, $n^{th}$ dilution),

$$\log_{10} C_n = \log_{10} C_0 + n \log_{10} \left[\frac{V_L - \nu}{V_L}\right]$$

Similarly, if it is assumed that there is a linear relation between absorbance and concentration,

$$\log_{10} A_n = \log_{10} A_0 + n \log_{10} \left[\frac{V_L - \nu}{V_L}\right]$$ ........................................ 5.9

where, $A_n$ is the absorbance of diluted solution after $(n+1)$ injections (that is, $n$ successive dilutions).

A plot of $\log_{10} A_n$ versus the number of dilutions, as in Equation 5.9, would be linear with slope $\log_{10} \left[\frac{V_L - \nu}{V_L}\right]$ and intercept $\log_{10} A_0$.

5.5.3. Procedure and results

The manifold in Fig. 5.7 was used. The spectrometer was operated with the settings for the determination of calcium at maximum sensitivity. The nebuliser liquid uptake at the settings was 8.0 ml min$^{-1}$. The absorbances for a 10 mg l$^{-1}$ calcium standard solution were measured through the following sequences:

(a), with both valves set at load positions, water was pumped through the valve connected to the peristaltic pump at 2.0 ml min$^{-1}$ whilst the syringe filled with the 10 mg l$^{-1}$ calcium solution was fitted to the arm of the second valve. The sample was drawn by pump action to fill the mixer loop (volume 640 µl);

(b), with both valves switched in unison to the inject position, 232 µl of the 10 mg l$^{-1}$ Ca was propelled to the nebuliser. This afforded the absorbance of the undiluted (except for manifold dispersions) 10 mg l$^{-1}$ Ca which was recorded at 60 s cm$^{-1}$; and

(c), with the valve connected to the pump in the load position, the 10 mg l$^{-1}$ Ca remaining in the mixer loop was mixed with water in a closed loop for 90 seconds. Then, an identical volume (23 2 µl) of the mixture was again propelled to the nebuliser as in (b).
The sequential repetition of (c) and (b) afforded the absorbances for the solution of calcium which was diluted till the spectrometer showed negligible absorbance.

This procedure was repeated for mixing periods of 60 seconds and 30 seconds. The results are shown in Table 5.7 and the basis of the plots in Fig. 5.8 is as explained previously (see section 5.5.2).

Table 5.7. Use of the manifold with closed-loop mixer to dilute a 10 mg l\(^{-1}\) calcium solution

<table>
<thead>
<tr>
<th>injection</th>
<th>dilution</th>
<th>Absorbances for circulation time for mixing :</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>90 s</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0.347</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.257</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>0.166</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>0.105</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>0.067</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>0.045</td>
</tr>
<tr>
<td>7</td>
<td>6</td>
<td>0.028</td>
</tr>
<tr>
<td>8</td>
<td>7</td>
<td>0.018</td>
</tr>
<tr>
<td>9</td>
<td>8</td>
<td>0.012</td>
</tr>
</tbody>
</table>

The trend of results predicted by the mathematical treatment of the data for absorbance and the number of dilutions are confirmed with the exponential and the linear plots shown in Fig. 5.8. A thirty seconds circulatory flow of the solutions, at a pumping flow rate of 2 ml min\(^{-1}\), was sufficient for a complete mix.

The least squares fit of the data points for the plot of \(\log_{10} A_n\) against number of dilutions/injections gave a slope of -0.1812. This value was substituted into Expression 5.5 to afford the value 1.52 as the dilution factor:

\[
slope = \log_{10} \left( \frac{(V_L - v)}{V_L} \right) = - \log_{10} \text{(dilution factor)} \quad ................. \quad 5.5
\]

where \(V_L\) is the volume of the closed-loop mixer; and \(v\), is the volume of the solution injected.
Fig. 5.8. Application of the close loop mixer to effect the serial dilution of 10 mg l⁻¹ calcium in manifold 5.7: injection of 232 μl aliquots into water carrier stream to the nebuliser at intervals of (▴), 30 s; (▪), 60 s; and (◎), 90 s. (I) and (II) are mathematical treatments of the conventional normal calibration curve. The nebuliser liquid uptake was 8.0 ml min⁻¹ and the pumping flow rate was 2.0 ml min⁻¹.)

The dilution factor calculated using the values 640 μl and 232 μl, which were experimentally determined as the volumes of the mixer and the sample loop in section 5.4.1, afforded 1.57 as the dilution factor. Both values of the dilution factor agree with each other with a relative error of 3%. This shows that the concentrations
of diluted solutions of a single standard solution, after each replicate injection, can be accurately determined. These concentrations together with the corresponding recorded absorbances would form the data for calibration purposes.

5.5.4. Discussion

In the literature, a closed-loop manifold configuration has been shown to be useful for repetitive determinations, dilutions and in situ reagent regeneration/recycling in FIA. However, the detector systems such as solution spectrophotometry and electrochemistry had been used.\textsuperscript{26-30} The flow-through cells for the detectors were incorporated within the loop such that the response from a single sample bolus could repeatedly be measured. Such arrangement was practicable because the measurement systems do not consume the sample contrary to sample consumption which obtains in atomic spectrometry. This work shows the logistics that permitted the closed-loop configuration to be effected outside the detector system, for FAAS. The devised procedure allowed the same volume to be injected repeatedly into the carrier stream whilst leaving the volume of the test solution unchanged. The closed-loop mixer when operated as devised has the potential for both normal and standard additions calibration strategies as well as having the advantages of FIA, especially with the use of small sample volumes. However, further experiments need to be designed in order to elucidate the merits of the closed-loop mixer in comparison with other FI- dilution techniques such as single standard calibrations with mixing chamber and zone penetration methods.

5.5.5. Conclusions

The closed-loop mixer could dilute a standard solution of calcium with a mechanism similar to the dilutions afforded with shaking in conventional flasks. These dilutions, obtained using a closed-loop mixer in FIA, would afford better precision than manual dilutions in flasks especially for small samples volumes. It would also afford faster analysis time.
REFERENCES

CHAPTER SIX

SUMMARY AND TRENDS

Flame atomic absorption spectrometry is used for the routine determination of trace metallic elements because it is largely free from spectral interference, is easier to operate and of lower cost in comparison with other atomic spectroscopic techniques such as ET-AAS, ICP-OES and AFS. Flame atomic absorption spectrometry, however, has poor detection power except in the case of mercury and hydride forming elements such as selenium. The determination of refractory elements in real samples could well be subject to considerable error because of solute volatilisation interferences from matrix components.

The mode of operation of the nebuliser-spray chamber-burner system in FAAS is a major factor in contributing to performance limitations. Improvements in the methods of sample introduction as well as nebuliser design could possibly improve the performance of the technique.

Sample introduction by FIA has been shown to permit introduction of samples with (a), concentrations of dissolved solids; (b), viscosity characteristics; and (c), solvent compositions that would normally cause unacceptable errors. The use of small sample volumes, as well as the fast and reproducible on-line treatments (physical and chemical) of samples, has been demonstrated to remove interferences and enhance sensitivity by the use of FI-AAS techniques such as on-line liquid-liquid extraction, ion exchange and in the work described earlier, precipitation-dissolution reactions. These procedures have been shown to isolate and simultaneously concentrate the analyte.

In Chapter 1, the emergence of FI-AAS with emphasis on FAAS was reviewed. The application of flame FI-AAS to the analysis of real samples such as clinical samples, environmental materials, foodstuffs, petroleum products and pharmaceutical preparations were outlined for the period 1986 to date. In this period, an upsurge in the development of on-line sample pretreatment rather than fast sample presentation to the nebuliser was noted. Methods for matrix conditioning and the resulting performances were given in section 1.3.

The conventional aspiration performance of the Baird-Atomic, Model A3400,
nebuliser system was studied, as well as with the use of forced flow. The results are given in Chapter 2. The adjustment of the capillary tip in the venturi throat was found to be critical for obtaining maximum sensitivity and maximum liquid uptake. An immediate problem observed for the instrument was the inadequacy of the drainage. Therefore the repeatability of the experiments in this report required the adaptation of the nebuliser to drain by suction, especially when working with low pumping flow rates (below 2 ml min$^{-1}$). The positions of the capillary tip for maximum sensitivity and maximum liquid uptake differed in the case of the determination of magnesium. The use of an external pump offered better control over the nebuliser uptake rate but the peristaltic pump roller pulsations showed as a periodic oscillation on the absorbance-time profile at low pumping rates. The amplitude of oscillation increased as the pumping flow rate decreased. The peak height sensitivity of FI-AAS with peristaltic pumping was similar, increased or lowered compared with that of conventional aspiration, depending on the sample volume, operating flow rate, the nebuliser capillary tip adjustment and the instrument response time constant. It was found that operation of the Baird-Atomic, Model A3400, spectrometer at the capillary tip position that offered maximum absorbance sensitivity, rather than maximum liquid uptake, gave improved signal to noise ratios with either conventional aspiration or controlled flow.

Peak height precision was not influenced by the inclusion of a pre-coil. However, an in-line air pulse damper (located prior to the injection unit) improved the signal to noise ratio by reducing the amplitude of the absorbance fluctuations. The effect was more pronounced for steady state profiles at low pumping flow rates (less than 2 ml min$^{-1}$).

In Chapter 3 it was demonstrated that the depressive effect of phosphate on the absorbance signal of calcium could be removed in a fuel-rich flame even for introduction by conventional aspiration. Introduction by FI could remove the depression, in both fuel-lean and fuel-rich flames, only at low pumping flow rates (below 2 ml min$^{-1}$). Increased nebulisation efficiency was obtained at the low flow rates but the reduced analyte mass transport resulted in low sensitivity. Moreover, the interference removal by FI was improved with the injection of small sample volumes. This indicates that the interference removal in FIA is also related to a dilution effect. Air compensation increased the dilution of the sample plug and reduced absorbance sensitivity, in comparison with that of continuous flow at a similar pumping flow rate. However, air compensation offered improved peak height precision over that obtained with continuous flow.
In Chapter 4, it was shown that the depressive effect of aluminium could only be removed by an on-line chemical reaction. A merging stream manifold was used. The selective precipitation of calcium oxalate was carried out at room temperature with an ammonia- ammonium oxalate reagent. The precipitate was dissolved in dilute hydrochloric acid. The dissolving solution was either injected or stream-switched. The depressive effect of a concentration of about 1 g l⁻¹ of aluminium on the absorbance of a 10 mg l⁻¹ calcium solution was completely removed. This removal was dependent on the characteristics of the in-line membrane filter. A filter diameter/retention volume greater than 5 mm/10 μl to permit a long wash without excessive back pressures in the manifold was required (see Table 4.10). However, the calcium sensitivity decreased as the filter diameter/retention volume increased. The manifolds shown in Figs. 4.22 and 5.1 produced results with an average relative percentage error of 5% for the determination of calcium in two slightly different samples of Portland cement and in synthetic solutions of the rock samples: "glass sand"; "glass soda lime sheet"; and "phosphate rock western".

Precipitation of calcium oxalate could also be used to give a high preconcentration factor of about 800 for a 10 ml test solution of calcium at μg l⁻¹ concentrations. The ammonia- ammonium oxalate reagent, used for the precipitation of calcium, was observed to enhance the sensitivity of calcium threefold. Therefore manifold designs should permit the reagent to saturate the nebuliser prior to the nebulisation of the sample plug for the repeatability of the experiments in this report. However, the slow reaction kinetics, that required low pumping rates (below 2 ml min⁻¹) to improve further the sensitivity of calcium, decreased the sample throughput when the manifold which incorporated a mixing T-junction was used.

In Chapter 5, the results of the use of a manifold with a closed-loop mixer as a reactor were given (see Fig. 5.5). It is suggested that the manifold could be suitable for use with on-line reactions of slow kinetics. The manifold was also used to estimate the solubility product of calcium oxalate. It was found that the closed-loop was a very efficient mixer which, in addition, was capable of dilution without limits (see Fig. 5.7). Preliminary results for the application of this manifold design for the dilution of a stock solution for calibration purposes were presented. A fixed volume of a standard solution of calcium was increasingly diluted (again to another fixed volume) as an identical injection volume was withdrawn at intervals for absorbance measurements. The corresponding concentration of the solution for each discrete dilution resulting from an injection act can be calculated using the dilution factor afforded by the closed-loop mixer. Therefore, the recorded absorbance- injection
profile could be transformed to an absorbance-concentration plot. This plot would then be used to determine the concentration corresponding to the recorded absorbance of an injected sample. The dilution factor is a ratio of the volume of the closed-loop and the injection volume and it is not affected by the liquid flow rate or the analysis delay time. The data collection with this method may not require computer control and the method is able to give absorbance signals at the delay times of 30 seconds or less at carrier flow rates of 2 ml min\(^{-1}\) and more. The in-situ dilutions would also permit the suitable dilution of a sample with an off-range concentration. Furthermore, the use of the manifold to dilute a sample solution with an interferent, would give absorbance signals at constant analyte to interferent concentration ratio. And the dilution that affords a low concentration of the interferent, or at which interference effects are removed, could be made.

In the literature, manifolds that have been used to generate calibration data from a single injection of a standard have applied the principles of gradient dilutions (see Fig. 6.1) afforded by zone sampling,\(^{1,2}\) continuous dilution in a mixing chamber,\(^3\) zone penetration\(^4\) and zone splitting ("network" manifold).\(^5\) The manifold with a mixing chamber is the simplest for it rapidly generates the calibration data. The manifold does not require computer control to give the continuous concentration time profile (see Equation 1 in Chapter 1) which in turn generates the absorbance-time response of the spectrometer. Data treatment with the use of the mixing chamber method does not require curve fitting approximations. However, the accuracy of the results depends on the: ideal performance of the mixing chamber; accurate measurement of flow rate and accurate recording of the residence times (in practice the recorded time zero-axis of the absorbance-time profiles may not be sharply defined). In addition, the calibration procedure does not offer an immediate dilution of off range samples. These characteristics of the mixing chamber method, as well as a magnetic stirrer assembly (which constitutes a bulky apparatus relative to the use of an additional valve for a closed-loop), are drawbacks relative to the use of the closed-loop method for calibration purposes.

The network manifold uses dispersions afforded by two or more different lengths of tubes between a split- and a confluence- junction for dilution purposes. The injection of a single standard solution into the carrier stream produces different dilutions, which are recorded as a composite absorbance-time profile of partially overlapping peaks. The procedure could give a high dilution factor and it does not require computer control. The dilutions could, however, be affected by the fluctuations in the carrier flow rate. Also the data points (three absorbance maxima/
(1), closed-loop Mixer:

(2), Mixing chamber:

(3), Zone-splitting ("network"): 

(4), Zone-sampling:

(5), Zone-penetration:

Fig. 6.1. The basic operations/features of the manifolds used, with a single injection of a standard solution, for dilution and calibration purposes in flow injection-atomic spectrometry.

(L, closed-loop; P, peristaltic pump; I, injection point; n-v, two nested 4-way rotary valves; s-v, slider valve; v, stream switching valve; MC, mixing chamber; std, standard solution; S, sample solution; B, sample stream by-pass; AAS and AES, spectrometer.)
peaks and two absorbance minima/ troughs for a three-branch network) are few and hence, the method was used for the determination of Mg, an element which shows a linear calibration graph in FAAS.

A two-line manifold with two injection valves was used by Reis et al.\textsuperscript{1} for zone sampling. In the procedure, portions of the dispersed sample zone from the first injection are reinjected at timed intervals into a second carrier stream. A high dilution (dispersion factor of 130) was reported but the dilutions are flow rate dependent and, moreover, require accurate timing which is preferably carried out with computer control if the dilutions are to be reproduced precisely. This could be why the dilutions are not applied for calibration purposes. Araujo et al.\textsuperscript{2} reported a variant of zone sampling technique, in which portions of the dispersed standard solution in a water carrier stream were merged with a pumped stream of sample solution. This variant was simpler to operate than the zone sampling with a double injector; and the authors used it to determine Ca, K and Na by FAES. The sample matrix was 0-10% ethanol and the error of the determination was less than 3% compared with the error of 42% in the conventional standard additions method. However, the limitation that the measurements are time dependent remained.

The zone penetration method reported by Fang et al. was used for calibrations by the method of standard additions in FAES.\textsuperscript{4} The method, called gradient standard additions, has been described in section 1.3.2. The mutual dispersions of a single standard and the sample zone in a water carrier stream gave the intensity-time profile. Again, a timing source is required in order to measure accurately the delay times of two points which have identical dispersions on the leading and tailing edges of the sample zone profile in a water carrier. The signal responses corresponding to these times are read off from the profile obtained for the zone penetrations (water/sample/standard) and are used with a derived equation to calculate the concentration of the sample.

In the work reported here, the manifolds (either with Y-junction or with closed-loop mixer) for the optimisation of the on-line precipitation of calcium oxalate were designed to overcome the shortcomings of an old spectrometer (Baird-Atomic, Model A3400). The low flow rate requirement for the precipitation needed the operation of the nebuliser with a liquid uptake rate lower than its conventional optimum uptake of about 5 ml min\textsuperscript{-1}. The operation of the nebuliser with a lower carrier liquid flow rate than the optimum liquid uptake, in the flow injection mode, improved nebulisation efficiency from about 10% to 30% without significant
nebuliser memory effects. However, the increased nebulisation efficiency does not give increased sensitivity due to the reduced analyte transport. Also, the base-line signal shifted with lengthy analysis times when a much reduced carrier flow rate (less than 0.5 ml min⁻¹) was used. The inadequate liquid-wash of the nebuliser-spray chamber-burner system most likely caused the salt deposits on the burner slot to vaporise and result in light scatter. This problem was avoided by the use of a separate stream line, from the liquid flow line that fed the nebuliser, for the precipitation. However, the flow rate requirement for the dissolution of the precipitates which also fed the nebuliser was still below the nebuliser optimum uptake. Hence, a reduced analytical sensitivity could not be avoided. In this respect, Tyson has demonstrated that a reduction in the nebuliser-spray chamber volume of such conventional spectrometers was needed to improve on sensitivity.⁶

Such an approach, involving the reduction in the dead volume of the spray chamber, was used by Kempster et al. for FI/ICP-AES.⁷ The function of the spray chamber to filter large aerosol droplets was maintained in the smaller design by centrifugal action. Consequently, the comparative study of this design with the conventional spray chamber showed two improved analytical characteristics in the determination of boron: (a), a 28% increase in sensitivity; and (b), an improved washout time/aerosol displacement time of less than 1 second at the carrier flow rate of 3.5 ml min⁻¹ (15 to 20 s for the conventional system). The detection limit for boron at a value of 0.5 mg l⁻¹, however, was degraded by two orders of magnitude which was explained by the authors as a limitation of the recording circuitry (instability present in the analogue signal output) rather than the ICP.

A different approach that involves the use of a heated spray chamber to generate small aerosol particles for the atomiser has been demonstrated to improve nebulisation efficiency, as well as to improve sensitivity for all carrier flow rates of a FI-AS coupling. The typical literature reports are: (a), the concentric nebuliser with heated spray chamber (CN-HSC) reported by Gustavsson;⁹ and (b), the thermospray nebuliser with heated spray chamber (TN-HSC) reported by Vermeiren et al.¹¹ The concentric nebuliser with heated spray chamber affords an analyte transport efficiency of 90% to 110% and the value is constant for all flow rates. This is due to the efficient desolvation afforded by the heated chamber which in turn rapidly produced small dry aerosol particles in comparison to the conventional nebuliser-spray chamber system. Whilst the solvent loading to the atomiser is minimised, the wide droplet size distribution generated by these devices definitely needs filtering so as to avoid an increase in solute volatilisation interferences.
compared to those arising with the conventional nebuliser-spray chamber systems. The results presented for the determination of Pb in blood by flame FI- AAS\textsuperscript{12} (see section 2.1) and the determination of tri- and di- butyltin species in wood preservatives by flame HPLC-AAS\textsuperscript{13} showed a 3 to 5 times improvement in detection limit, compared with those obtained with conventional nebulisation. A carrier/eluent flow rate of about 2 ml min\textsuperscript{-1} was used. However, there are yet no reports on the possible interference effects that could result from the CN-HSC interface in FAAS.

The TN-HSC system, when applied in FI/ICP-AES, was demonstrated to afford: (a), a 15 times lower detection limit compared to a conventional pneumatic nebuliser-spray chamber (without heating); and (b), a 3 times lower detection limit compared to normal TN-SC (that is, without heating the spray chamber). But, increased matrix effects which were also observed, were claimed to be a direct effect of heating the chamber. The matrix effects could, as well, be a result of the application of heat to the sample solution in the nebuliser; this has been found to cause pre-boiling and erratic nebulisation.\textsuperscript{14} Therefore, a pneumatic nebuliser coupled with a spray chamber of reduced dead volume would be a suitable interface needed to improve the sensitivity, in flame FI- AAS. There is a need to evaluate the minimum effective dead volume which would give high sensitivity without deterioration in the signal noise and hence in detection limit. Studies that involve the variation of the dimensions of a cylindrical spray chamber are reported recently for discrete and continuous nebulisation procedures in ICP-AES.\textsuperscript{15} The spray chamber and/or the aerosol could be heated (heating only the aerosol with infrared radiation) for an additional increase in sensitivity. This would require suitable liquid flow rates for the nebuliser wash so as to overcome salt deposits and drift in signal output. As an alternative, additional increase in sensitivity may be achieved by the differential diffusion of the solvent vapour through a membrane separator as described by Gustavsson for ICP-AES.\textsuperscript{9,16}

Sample introduction to nebulisers by FI will continue to generate interest for it permits the sample feed rate to be controlled independently from the nebuliser and the atomiser operating parameters such as oxidant and fuel gas flow rates.

**SUGGESTIONS FOR FURTHER WORK**

The success of the findings of the present report are largely due to incorporation of a
filter unit capable of continuous precipitate gathering. The precipitate used, calcium oxalate, is normally considered difficult to filter because the crystals readily clog the pores of a filter. In a continuous precipitation manifold, this would generate excessive back pressures that would eventually cause leaks. Therefore, the design of the significant manifold features needs to be improved in applying the precipitation manifold to solve analytical problems.

Design of the filter units It was found that excessive back pressure decreased for large filter diameters/retention volumes and was completely removed when a minicolumn of packed inert materials was coupled to a membrane filter. The filter units allowed the precipitates to accumulate by a graded collection of precipitates. Therefore compact filter units designed specifically for FI-precipitations are necessary. Some proposed designs are presented in Fig. 6.2.

Fig. 6.2. Proposed in-line filter units.
(1), uniform pore membrane filter;
(2), different uniform-pore membrane filters in a composite pack with pore size increase from left to right;
(3), tubular membrane filter; and
(4), open tubular membrane in a crossed-flow.
[outer casings of the filters could be fabricated in polymer plastics.]

The units are similar in shape to the existing "syringe" filters and the filters in use in HPLC. However, smaller dimensions are required. The filter diameter should be smaller than 10 mm to give improved sensitivity; the retention volumes on either side of the membrane should be a few microlitres to improve the solid-solution contact
needed to dissolve the precipitate. The membrane and housing could be fabricated from an organic polymer material to reduce costs and contamination. Accurate machining may not be essential.

**Design of mixers** There are numerous precipitation-reactions described in the literature, many of which involve metal ions, for the gravimetric determination of either cations or anions in both organic and inorganic analysis.\(^{17,18}\) No kinetic restrictions on such reactions are apparent as the reactions could be fast or slow. The precipitation of copper hydroxide was sufficiently rapid, for an FI- manifold incorporating a merging tee could produce mixing of the reactants at both low and high flow rates.\(^{19}\) The precipitation of calcium oxalate and other similar reactions of slow kinetics are possibly best carried out in the manifold with the closed loop mixer (shown in Fig. 5.2). Otherwise, the merging tee could require low pumping flow rates to increase residence time and a hold-up volume at its confluence point to be an efficient mixer unless another mechanism such as tortuous flow or sonication is used. Therefore the manifold shown in Fig 5.2 (including one pump two four-way and one three-way rotary valves) should perform well with different reaction kinetics. Automation could readily be achieved by electronic valve actuation.

**Analytical schemes**

Manifolds designed for on-line precipitation/dissolution could be adapted to the determination of:

(a), *an analyte in the filtrate*; in which case, the unwanted solids could be chemically dissolved at intervals or back-flushed to reduce excessive back pressures in the manifold. Back flushing could be facilitated if the filter is positioned in the injection loop of a four-way rotary valve as described for the regeneration of ion exchange columns by Bysouth and coworkers.\(^{20}\) The bores within the valve would however, have to be enlarged to avoid blockage. The incorporation of crossed flow as proposed with filter 4 could offer a better alternative for the solids to pass on to waste.

(b), *an analyte in the precipitate* would require rapid dissolution of the precipitate to be effected with a suitable solvent.

Scheme (a) could be applied for interference removal, where the solubility product of the interferent is very low. Otherwise, the use of a mixed solvent medium, such as the addition of ethanol to aqueous mixtures, may be required. Scheme (b) could also be applied for interference removal with precipitate washing and also for
preconcentration. These schemes should be combined with the optimum conditions for the precipitation of calcium oxalate in Chapter 4 to form the basis of the following applications of the manifold, shown in Fig. 5.2, for multi-element and speciation studies.

**Group-precipitation of alkaline earth oxalates** The alkaline earth elements (magnesium, calcium, strontium and barium) all form insoluble oxalates. Therefore, the procedure used for the determination of calcium by the precipitation of calcium oxalate followed with acid dissolution could also be applied for the individual determination of the other alkaline earths (see section 4.5). Also, an analysis solution containing two or more of the cations when put through the precipitation-dissolution procedure would give a group precipitation of the cations which are soluble in dilute hydrochloric acid. Since these elements do not interfere with one another in FAAS, then, one element could be determined in the presence of another as long as the spectrometer is set for the determination of the element of choice. Hence, sequential multi-element determination of the cations could be carried out by the repeated injections of a single stock sample solution. However, the test elements should be present as major constituents in the sample solution containing foreign ions such as iron, manganese and chromium so as to minimise the effect of the coprecipitation. This effect caused negligible signal for calcium by the oxalate precipitation in section 5.3.1 (see Tables 5.2 and 5.3).

The merits of such group precipitations should be evaluated with a preliminary experiment designed to study: (a), the effect of precipitation time; and (b), the effect of varying the concentration ratio of the constituent cations in a synthetic test solution; on the precipitate yield and hence on the analytical range and sensitivity for each element. It is suggested that the manifold with a closed-loop mixer be used for the experiments (see Figs. 5.5 and 5.6 in Chapter 5).

A recent report by Broekaert\(^{21}\) included a description of commercial flame spectrometer which has a simultaneous multi-element capability. The spectrometer incorporates up to twelve hollow cathode lamps, so that the radiation response from up to twelve elements may be entered through fibre optics for detection. Such a spectrometer would permit the simultaneous multi-element determination of the alkaline earths through the group precipitation of their oxalates from a single injection of the sample solution. Again, the analytical merits need to be evaluated with the use of synthetic mixtures of the cations. Then, the experimental procedures can be carried out for the determination of alkaline earths in real samples such as
natural waters, industrial water effluents, rocks, soils, fertilizers, etc., for further assessment.

Precipitation of calcium oxalate from homogeneous solutions. The coprecipitation of the trivalent cations (Fe(III), Cr(III), Mn(III), etc.), when present in a sample matrix of calcium, have commonly been prevented in classical gravimetric analysis by the addition of complex-forming agents to the sample solution. Ethylenediaminetetraacetate (EDTA), citrate, salicylate and gluconate ions have been used. These ions form strong complex compounds with the trivalent cations which do not interfere with the precipitation of calcium oxalate in an ammoniacal medium at room temperature.\textsuperscript{17,22,23} In this work, however, the use of EDTA and citrate ions as complexing agents could not produce signals for calcium in calcium oxalate precipitates, when the procedure was adapted into an FI-precipitation-dissolution procedure (see section 5.3). It could be possible that a slow precipitation of calcium oxalate from a homogeneous solution of urea with ammonium oxalate, in the presence of the complexing agent, would resolve the problem. Therefore, it is suggested that a heating unit, with a thermostat control, be located in the closed-loop mixer for the purpose of gradually raising the temperature of the reaction mixture so as to effect the hydrolysis of urea. The manifold shown in Fig. 5.5 should be used. The ammonia generated would slowly increase the pH of the reaction mixture to precipitate calcium oxalate with minimal coprecipitation of the trivalent cations. When these trivalent cations are in large excess in the sample matrix, the incorporation of a microcolumn of cation exchange resin or a flow-through electrodeposition cell located in the sample flow line should remove the excess trivalent cations. The sample effluent from the column/cell would then be injected accordingly for oxalate precipitation. The additional ion-exchange or electrochemical features may be necessary to remove excessive coprecipitation interferences if the high enrichment factors for the preconcentration of ultra-trace amounts of calcium by the calcium oxalate precipitation is to realised (see section 5.3). However, these additional features would add to the complexity of the precipitation manifold so that the determination of calcium, when present in more than trace amounts in a sample, might be carried out more effectively by simple FIA with lanthanum addition.

The merits of the homogeneous precipitation procedure should be evaluated with the determination of alkaline earth in some real samples such as clinical samples; calcium rock, minerals, ores and alloys: including iron, manganese, chrome ores.
Determination of available lime (as CaO) in calcium rock In the conventional method, a pulverised sample of lime rock (containing CaO, CaCO₃, CaSO₄, CaF₂, etc.) is shaken with a sugar solution when only the CaO component dissolves as it forms a water soluble calcium saccharide, \((\text{C}_{12}\text{H}_{22}\text{O}_{11}.\text{CaO.2H₂O})\). The mixture is filtered and the calcium determined in the filtrate. This analysis is of utmost importance in industries, such as those involving paper and food production, where lime is used as a cheap base in chemical processes.

The circulatory liquid flows in a closed-loop mixer should permit the above experiment to be adapted to FIA. In this case, the circulatory flow is expected to cause partial or complete solubilisation of a solid sample with a suitable reagent. It is suggested that the solid be turned into a slurry so as to afford a trouble-free introduction into the closed-loop mixer as well as to aid solubilisation. The manifold shown in Fig. 6.3 is proposed for use in the experiment.

![Fig. 6.3. Proposed manifold for the determination of calcium oxide species in a lime rock sample.](image)

C, water; R, sugar solution reagent; S, sample slurry; M, magnetic stirrer; L, circulation loop-mixer; I, injection port for the dissolution of solid residues; m, minicolumn of polystyrene granules; f, packed PTFE membrane (0.2 μm pore-size, 5 mm i.d.); v1, two nested 4-way rotary valves as stream selector; v2, stream-switching valve; and AAS, flame spectrometer.

The operation of the nested valves in the manifold is similar to the description applied for a closed-loop mixing in Chapter 5 (see Fig. 5.6). Therefore, the operation sequences for the procedure for the FIA-determination of available lime in a sample of calcium rock would be:
(a), pump the sugar solution to fill the mixer; (b), pump the slurry, only, to fill the injection loop; (c), circulate the mixture for a timed period; (d), pump the sugar solution to propel the reaction mixture through the filter unit to the spectrometer for absorbance reading; and (e), repeat the sequence from (b).
Whilst the reaction mixture circulates in the mixer, water flows through the filter unit to the nebuliser. During this operation, inject dilute HCl to dissolve the CaCO\textsubscript{3} residues (record the absorbance if CaCO\textsubscript{3} species is to be determined); then inject solution of ammonium chloride to dissolve CaSO\textsubscript{4} (record the absorbance if CaSO\textsubscript{4} species is to be determined);\textsuperscript{22} and finally inject boric acid-nitric acid solution to dissolve CaF\textsubscript{2} (record the absorbance if CaF\textsubscript{2} species is to be determined).\textsuperscript{23} The calibration graph/s (absorbance against mass of species in one unit volume of slurry) should be prepared using the slurry forms of the standards put through similar FI- procedure. The composition of the species in the sample slurry would be read off from the corresponding calibration graph. This value, relative to the make-up mass per unit volume of sample slurry, gives the proportion of the species in the lime rock sample.

For this experiment, the slurry may be prepared by grinding the sample and wet sieving to obtain particle-sizes considerably larger than the membrane filter pore (0.2 \( \mu \)m) and less than the bores of the manifold tubings and valves. An ethanol/glycerol mixture and a Triton X-100 solution may be used as dispersing and wetting agents.\textsuperscript{24,25} The effect of the particle size of the slurry on the analysis time and analytical characteristics of calcium should be studied.

In conclusion, considerable additional development still remains in the following areas:
(a), method development for the indirect determination of anions. The ammoniacal solution of calcium ions should serve for the precipitation of anions such as oxalate, sulphate, carbonate, fluoride and molybdate; and
(b), the development of hardware and software for computer control of the operations in the precipitation manifold.

It is now five years since Tyson\textsuperscript{26} predicted that FI- techniques could open up the area of indirect methods in routine FAAS. With the design of suitable manifolds, such procedures could be reduced to the action of filling the sample loop and actuating the injection valve. The manifold shown in Fig. 5.5 fits such a description for conducting on-line precipitations.
REFERENCES

### APPENDIX (I)

**List of abbreviations to Journals**

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<thead>
<tr>
<th>Journal Name</th>
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**APPENDIX (II)**

**BOOKS/periodical for FLOW INJECTION ANALYSIS**


* a section on FIA